FINAL REPORT

Environmentally Friendly Zirconium Oxide Pretreatment

SERDP Project WP-1676

MAY 2013

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE *(DD-MM-YYYY)* 01-08-2013	2. REPORT TYPE SERDP Project Final Report	3. DATES COVERED *(From - To)* July 1, 2009 to December 31, 2012

4. TITLE AND SUBTITLE

SERDP-1676 Environmentally Friendly Zirconium Oxide Pretreatment.

5a. CONTRACT NUMBER
W912HG-09-C-0038

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER
WP-1676

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and
Development Program (SERDP)
901 North Stuart Street
Suite 303
Arlington, VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Pretreatments based on zirconium oxide are being used commercially in automotive and other industrial operations as replacements to hexavalent chromium-based and zinc phosphate pretreatments. This report describes work to document the performance of commercial zirconium oxide pretreatments when used with existing military primers and, where necessary, to modify them to meet military specifications for performance.

The evaluation of zirconium immersion pretreatments intended for OEM application over CRS and aluminum with water-borne and solvent-borne Mil-Spec primers gave results in corrosion performance similar to the chrome (VI) and zinc phosphate pretreatment controls. In conjunction with ARL, modified versions of the commercial zirconium pretreatment were developed that showed corrosion resistance equal to or better than zinc phosphate in both spray-applied and immersion-applied processes. Therefore, the work showed that the current commercial zirconium pretreatment technology with some modifications is suited for use in DoD OEM processes. Visits to Marine Corps Logistics Base Albany, Albany GA, and Letterkenny Army Depot, Chambersburg PA, suggested that development of an immersion zirconium pretreatment process would be of utility for DoD repair depots as well.

However, many painting operations that are used by depots or in field repair settings, which could benefit from the use of zirconium pretreatment technology, require spray application, with or without a subsequent rinse. Versions of zirconium pretreatments based on the currently commercial systems were tested as a Spray-On/Rinse-Off treatment or as a Dried-In-Place (DIP) treatment. By adding a rheology modifier to a spray version of the OEM product to hold the pretreatment on the intended part during reaction, a Spray-On/Rinse-Off product was developed which demonstrated good corrosion and adhesion performance under CARC primers. In addition, several versions of a Dried-In-Place zirconium treatment were developed that gave improved corrosion performance by the addition of either an organic-modified inorganic metal salt compound or by using an alternative source of zirconium ions.

The work of this project suggests that zirconium oxide-based pretreatments can be successfully used as a replacement for zinc phosphate and chrome conversion coating pretreatments and chrome (VI)-based wash primer in either an OEM application or in field settings, enabling the DoD to comply with current and future environmental regulations, enhancing worker safety, reducing waste generation, and potentially reducing overall cost.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Nathan J. Silvernail
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**		72	**19b. TELEPHONE NUMBER** *(include area code)* 412-492-5708

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Table of Contents

List of Figures

List of Tables

ACRONYMS

ARL	Army Research Laboratory
ASTM	American Society for Testing and Materials
AVCRAD	Aviation Classification Repair Activity Depot
Chrome (VI)	Hexavalent Chromium
CRS	Cold Rolled Steel
CARC	Chemical Agent Resistant Coating
DoD	Department of Defense
DMA	Dynamic Mechanical Analysis
DIP	Dried-In-Place Pretreatment
EDS	Energy-Dispersive X-ray Spectroscopy
FZA	Hexafluorozirconic acid
GMW14872	General Motors (Corporation) World Specification 14872
HAP	Hazardous Air Pollutant
HHA	High-Hard Armor
JP8	Jet Propellant 8 jet fuel used by the US Military
OEM	Original Equipment Manufacturer
PATTI	Pneumatic Adhesion Tensile Testing Instrument
SEM	Scanning Electron Microscope
SERDP	Strategic Environmental Research and Development Program
VCI	Volatile Corrosion Inhibiting
XPS	X-ray Photoelectron Spectroscopy
XRF	X-ray Fluorescence Spectroscopy

KEYWORDS

adhesion, aluminum, CARC, corrosion, dried-in-place, depot, environment, hexafluorozirconic acid, hexavalent chromium, paint, pretreatment, primer, steel, TT-C-490E, Zircobond, zirconium

ACKNOWLEDGEMENTS

ABSTRACT

Pretreatments based on zirconium oxide are being used commercially in automotive and other industrial operations as replacements for hexavalent chromium-based and zinc phosphate pretreatments. This report describes work to document the performance of commercial zirconium oxide pretreatments when used with existing military primers and, where necessary, to modify them to meet military specifications for performance.

The evaluation of zirconium immersion pretreatments intended for OEM application over CRS and aluminum with water-borne and solvent-borne Mil-Spec primers gave results in corrosion performance similar to the chrome (VI) and zinc phosphate pretreatment controls. In conjunction with ARL, modified versions of the commercial zirconium pretreatment were developed that showed corrosion resistance equal to or better than zinc phosphate in both spray-applied and immersion-applied processes. Therefore, the work showed that the current commercial zirconium pretreatment technology with some modifications is suited for use in DoD OEM processes. Visits to Marine Corps Logistics Base Albany, Albany GA, and Letterkenny Army Depot, Chambersburg PA, suggested that development of an immersion zirconium pretreatment process would be of utility for DoD repair depots as well.

However many painting operations that are used by depots or in field repair settings, which could benefit from the use of zirconium pretreatment technology, require spray application, with or without a subsequent rinse. Versions of zirconium pretreatments based on the currently commercial systems were tested as a Spray-On/Rinse-Off treatment or as a Dried-In-Place (DIP) treatment. By adding a rheology modifier to a spray version of the OEM product to hold the pretreatment on the intended part during reaction, a Spray-On/Rinse-Off product was developed which demonstrated good corrosion and adhesion performance under CARC primers. In addition, several versions of a Dried-In-Place zirconium treatment were developed that gave improved corrosion performance by the addition of either an organic-modified inorganic metal salt compound or by using an alternative source of zirconium ions.

The work of this project suggests that zirconium oxide-based pretreatments can be successfully used as a replacement for zinc phosphate and chrome conversion coating pretreatments and chrome (VI)-based wash primer in either an OEM application or in field settings, enabling the DoD to comply with current and future environmental regulations, enhancing worker safety, reducing waste generation, and potentially reducing overall cost.

OBJECTIVE

The objective of this project was to evaluate and adapt existing zirconium oxide-based pretreatment systems (trademarked by PPG as Zircobond®) for DoD use in OEM production, depot application, and field application, in order to eliminate the use of regulated heavy metals, such as chrome (VI) or Ni, and replace phosphate-based pretreatments, which generate by-products that are environmental hazards.

A work plan was developed which involved benchmarking the performance of commercial zirconium oxide-based products against military specifications and, where necessary, modifying these products to meet the specification and application requirements. The

challenge in this work was to provide the level of corrosion protection and paint adhesion provided by the incumbent chrome (VI) and zinc phosphate technologies over all substrates used by the DoD, including commercial quality cold rolled carbon steel, 7075-T6 and 2024-T3 aluminum, and commercial quality 70/70 hot-dipped galvanized steel.

Pretreatments based on zirconium immersion and spray pretreatment platforms have been under development at PPG Industries, Inc. for 15 years and have been in commercial use for 5 years.[1] Prior to the initiation of SERDP-1676, discoveries were made which led to the ability to produce a high-quality, continuous zirconium-based pretreatment film over multiple types of ferrous, zinc, and aluminum substrates by immersing or spraying the metal in a dilute solution of hexafluorozirconic acid (FZA) and a proprietary copper salt. This pretreatment has been shown to provide corrosion performance comparable to tricationic zinc phosphate systems on all automotive substrates (cold-rolled steel, galvanized steel, and aluminum). Further, zirconium oxide pretreatment systems have been implemented at automotive OEM body lines for 5 years with >5 million cars currently in the field. While the corrosion performance has been shown to be similar to zinc phosphate technology, automotive OEMs have realized several environmental and cost benefits such as reduced water usage, ambient operation, reduced footprint, and greatly reduced sludge generation.

Therefore, coatings based on zirconium pretreatments may provide performance similar to incumbent technologies with environmental benefits to the DoD. This project was carried out to document the performance of commercial zirconium-based immersion and spray pretreatments with existing military primers, and if necessary, modify them for DoD use (See **Figure 1** for description of application methods). Additionally, work was carried out toward the development of a Dried-In-Place pretreatment based on zirconium for direct replacement of chrome (VI) wash primers.

Figure 1. (a) Immersion application of zirconium pretreatments. (b) spray application of zirconium pretreatments. (c) Dried-In-Place application of zirconium pretreatments.

The technical goal of this project was to develop and optimize a zirconium-based surface treatment with the following attributes: 1) ease of application using existing spray and immersion methods with minimal infrastructure modification, 2) performance equal to (or better than) existing chrome (VI) wash primers, 3) broad compatibility with the current suite of military coatings (including solvent- and water-based primers and top coats), and 4) compatibility with a broad range of substrates. During the execution of the project, it was apparent through interactions with ARL and the depots described below that added objectives might provide additional benefit the DoD. These objectives included evaluating novel pretreatment systems for

performance against zinc phosphate pretreatment, and supporting ARL during the modification of the TT-C-490E specification.[2]

BACKGROUND

Approved processes to prepare surfaces for painting Department of Defense articles, such as tactical vehicles and munitions, include the use of materials that present environmental and human health hazards, including, but not limited to, chrome (VI)[3], heavy metal compounds[4], volatile organic solvents, and phosphoric acid or salts[5] thereof. In addition, these processes can produce other waste by-products, such as phosphate sludge, which may contain metals such as manganese, cobalt, nickel, and/or zinc. These by-products must then be disposed of, generating more potential environmental hazards and disposal costs. Therefore, there is a need to develop and introduce chemical processes that minimize these environmental and health hazards. The objective of this project was to develop zirconium oxide based pretreatment technology and demonstrate that it meets the requirements and needs of the DoD to manufacture and maintain vehicles and equipment in a manner that meets environmental and health requirements, while maintaining the ability to meet DoD corrosion-resistance requirements for coated assets as described in MIL-DTL-53022 and MIL-DTL-53030 for epoxy primers

The application of organic coatings to metal substrates requires the cleaning and treating of metal surfaces in order to take advantage of all of the performance characteristics of the coating. The cleaning process removes oils, organic contaminants, and oxidation from the surface. The pretreatment is applied to provide a thin-film coating to which the paint can tightly bind. The pretreatment can also provide a modicum of corrosion protection, though not enough to protect the substrate by itself. For example, cold-rolled steel which is painted, even with a high performing primer system such as cationic electrocoat, must be coated with a pretreatment after cleaning and prior to primer application. In summary, in the absence of a pretreatment, the coating system performs poorly (see **Figure 2**).

No pretreatment   Zinc phosphate pretreatment
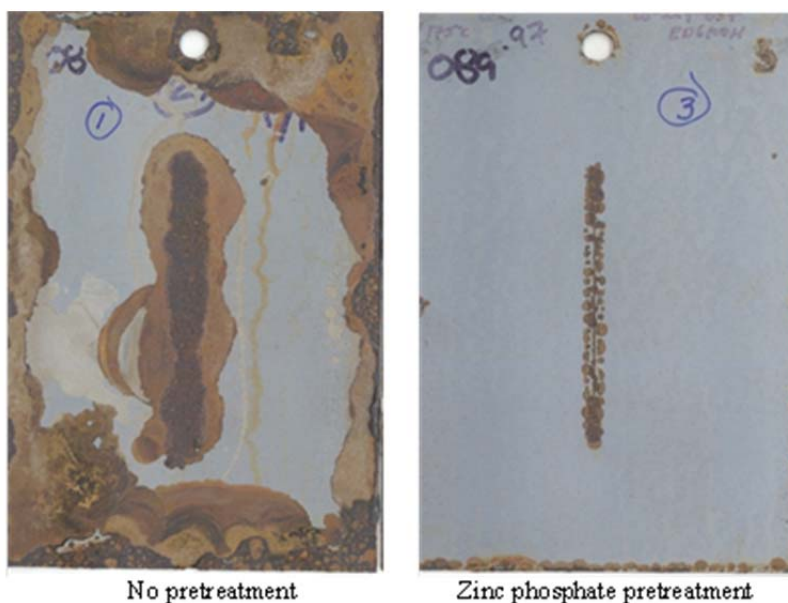
Figure 2. GMW14872 Corrosion Testing of CRS, with and without zinc phosphate pretreatment and coated with cationic electrocoat.

Metal treatments typically used for industrial and military applications are based on iron phosphate, zinc phosphate, or chrome (VI) pigmented wash primers. In some cases a wash primer containing a zinc or strontium chromate pigment system and a resinous binder functions as both a metal treatment and primer. Each process has drawbacks associated with a possible negative impact on either the health of workers due to processing or rework exposure or a negative impact on the environment due the use of HAPs or other regulated materials in the formulation (See **Figure 3**).
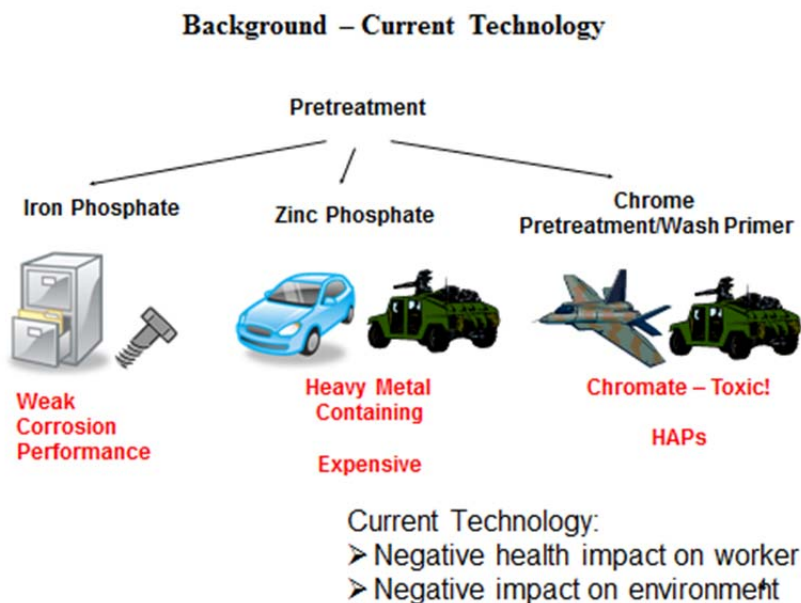
Figure 3. Drawbacks to Current Surface Preparation Technology Used in Military Painting

Like chrome (VI) treatments, phosphate pretreatments also have several drawbacks. During the reaction of the zinc phosphate solution with metal substrates, an insoluble precipitate or sludge is generated. This sludge typically contains compounds of iron, zinc, manganese, nickel, and phosphate, as well as oil. Due to the nickel (a regulated metal) content, special handling and disposal of the sludge is necessary. The high cost of this special disposal process adds to the overall operational costs. Attempts to commercialize processes that separate and recycle the components of the sludge have not been successful, due to the high amount of oil present and the cost to remove it. Thus, industry has increasingly come to the realization that the health and environmental impacts as well as the high disposal costs make the replacement of zinc phosphate pretreatments a necessity.[6]

An alternative to metal phosphates has been developed and commercialized which has been shown to provide corrosion performance that is comparable to tricationic zinc phosphate systems on all automotive substrates (cold-rolled steel, galvanized steel, and aluminum). Zirconium oxide based metal treatments have been commercialized in the general industrial and automotive industries as replacements for metal phosphates. These pretreatments have been commercial since 2008 in Automotive OEM body lines, and prior to that in General Industrial manufacturing. There are currently > 5 million automobiles using this technology. Automotive

OEMs have used this technology as an "environmentally responsible, cost-effective, high-performance pretreatment."[1]

These novel pretreatment systems based on zirconium oxide have several advantages over the previous technologies. For example, the footprint of the new pretreatment technology is reduced when compared to zinc phosphate. **Figure 4** compares the zinc phosphate process and the zirconium oxide application. As shown in the diagram, the phosphate process may contain up to 11 steps, including a post rinse or sealer, which may contain chrome (VI). The zirconium pretreatment process has 8 steps, and therefore has a smaller footprint in the operation. Footprint reduction is possible because the reaction that deposits zirconium oxide at the metal surface differs from that of zinc phosphate. Both reactions require microcathodic and microanodic sites to impose a potential across the surface leading to the reduction of H_2O and formation of hydrogen gas and OH^- (hydroxide) at the microcathode and O_2 and H^+ (acid) at the microanode.[7]
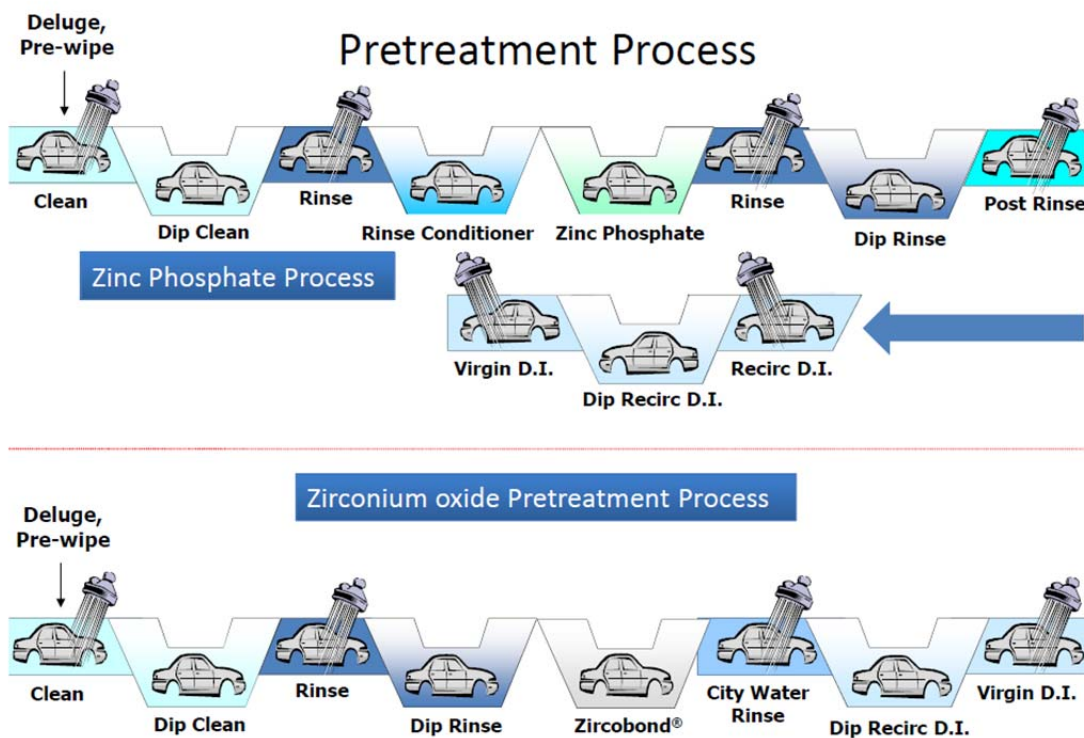
Figure 4. Comparison of Zinc Phosphate and Zircobond® Pretreatment Processes.

This reaction leads to the formation of a gradient of increased pH at the substrate surface. Both zinc phosphate and zirconium pretreatments are stable under bath conditions, however, as the area near the surface increases in pH the zirconium or zinc phosphate materials become insoluble, subsequently coating the surface. The two pretreatments differ, however, because there is a secondary driving force to the deposition of zinc phosphate which is not present in zirconium pretreatments. Zinc phosphate pretreatments are deposited not only by destabilization due to higher pH at the surface, but also the formation of a crystalline coating (unlike zirconium pretreatments, which are amorphous; see **Figure 5**). Uniform deposition of the crystalline zinc

phosphate pretreatment requires the use of an activator step (or rinse conditioner) prior to pretreatment deposition.[8] This step promotes the homogenous nucleation of small zinc phosphate hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) or phosphophyllite ($Zn_2Fe(PO_4)_2 \cdot 4H_2O$) crystal morphologies. This nucleation step is eliminated in the zirconium pretreatment process. Work prior to this contract by PPG and others[9a,b] has shown that the addition of an electropositive metal such as copper directly to the zirconium pretreatment can help improve the morphology and properties of the zirconium oxide coating without the need for a separate activator step. This metal additive was found to be essential for good performance when the zirconium pretreatment was used in conjunction with cathodic electrocoat.[10,11] However, the work conducted under this program indicated that the metal additive may not provide the same benefit when immersion zirconium treatments are used with DoD coatings. Improved performance was achieved when the zirconium pretreatment was utilized without this additive.
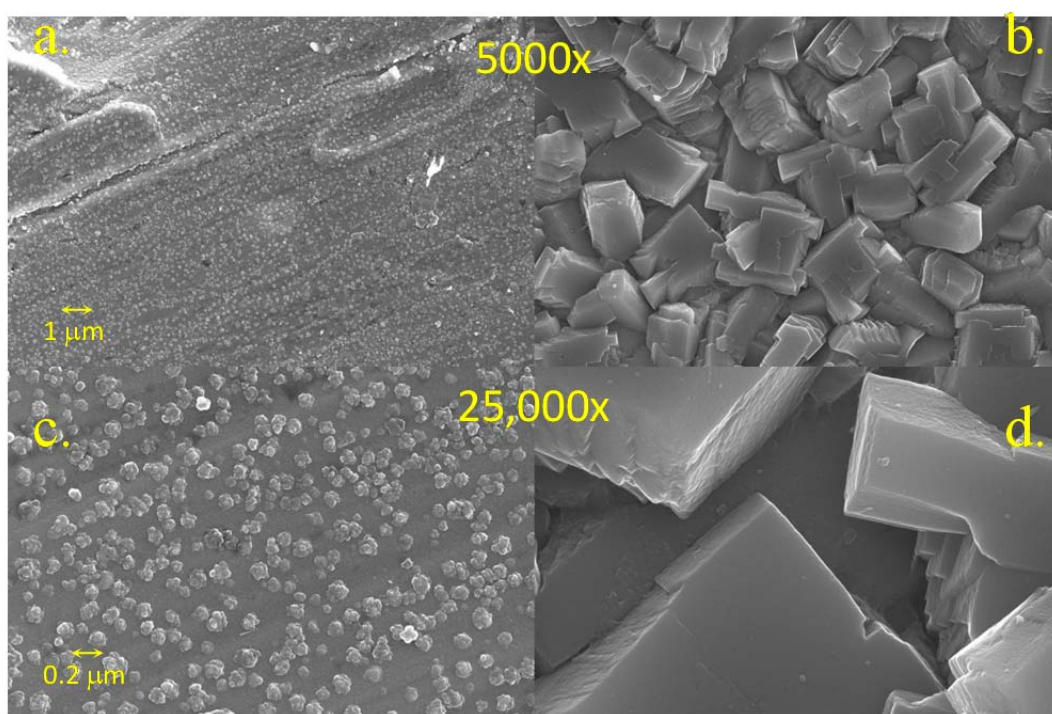
Figure 5. (a) Zirconium-based pretreatment SEM image at 5,000x magnification. (b) Zinc phosphate pretreatment SEM image at 5,000x magnification (c) Zirconium-based pretreatment SEM image at 25,000x magnification. (d) Zinc phosphate pretreatment SEM image at 25,000x magnification.

Additional reductions in footprint are garnered from the elimination of the post rinse or sealer step which follows zinc phosphate. The sealer step is usually based on chromium or zirconium chemistries and is intended to coat interstitial spaces between crystals, and to provide a more insoluble layer at the crystal surface.[12] Because zirconium pretreatments are uniform, and amorphous, the sealing step is unnecessary to achieve good corrosion resistance.

In addition to the footprint reduction, there are several additional benefits of the zirconium pretreatment system. Zinc phosphate (and occasionally metal activator/rinse conditioner) steps take place at higher temperatures, above 100°F. Further, some metal

phosphate systems operate as high as 180°F. Zirconium-based pretreatments have been designed to operate at room temperature. Consequently the zirconium process can reduce energy and water consumption, thereby reducing the processing cost and environmental impact. Zirconium pretreatment baths also operate at a higher pH than traditional zinc phosphates. Finally, zirconium pretreatments are simpler to operate than traditional zinc phosphate baths due to the reduction in bath complexity. Zirconium pretreatment baths are <1% solids, and are controlled using a pH probe and a metering pump (additional tests may be necessary to insure optimal performance).

THEORY AND METHODOLOGY FOR SCREENING PERFORMANCE

To maximize the efficiency in which zirconium formulations could be benchmarked and, if necessary, improved to yield optimum performance with DoD substrates and coatings, a number of factors were taken into consideration. It was quickly decided that good adhesion of the pretreatment(s) to the substrates as well as to the coatings would be critical. Correspondingly, a screening test methodology would need to be utilized that could correlate with other requirements and provide the best chance of successful specification testing. To select the best and most efficient screening methodology, it was necessary to understand some basics about adhesion of coating systems and how it could correlate to other performance criteria.

First, overall performance is dependent on all interactions within a system and the mode of failure will often be at the point of weakest bonding interactions and / or highest (potential) chemical activity. In other words, the durability and performance of a coating system under a variety of environmental conditions is dependent on both the strength of molecular bonds within each film layer as well as the adhesive bonds between layers.

Second, for most thin film layers such as crosslinked coatings and amorphous/crystalline inorganic pretreatments, intermolecular forces within the layer are often significantly stronger than interfacial adhesive forces.[13] This is due to the fact that the covalent, ionic, and / or cohesive bonds (such as hydrogen bonding) within layers of like molecules are much stronger and more numerous than the bonding forces (such as van der Waals forces, London forces, mechanical interactions, etc.) that are often found between layers of unlike molecules.

Third, however, when interfacial interactions are able to utilize stronger bonding schemes such as ionic or hydrogen bonding, the bonding of the entire system is often enhanced, sometimes significantly. Thus, modifications that promote stronger interfacial bonding schemes can yield overall improved performance.

Fourth, as discussed above and elsewhere[14], a pretreatment with the ability to strongly bind to the underlying substrate and the overlaying coating is often key to the performance of the whole coating system. In order for a pretreatment to interact with two chemically distinct layers (metal/metal oxide and organic coatings), it must have functional groups that interact with both layers. In general, organometallic compounds or compounds containing bridging oxides (μ-oxo compounds) have been found to work well as pretreatments. Metal-alkoxides, silica sol-gels, metal phosphates, chromates and zirconium pretreatments all fall into these categories. Although the deposition mechanism of each of these pretreatments varies from hydrolysis to crystalline conversion coating, and from a thermodynamically driven redox reaction to a simple

surface metathesis, each has one thing in common – the formation of a new layer containing a metal oxide or a metal oxide salt which is chemically integral (bonded) with the substrate and able to further react with organic coatings.   Understanding of this concept was key to designing experiments for further improvement of adhesion and other performance characteristics.

Lastly, successful deposition of a viable pretreatment is often highly dependent on proper surface preparation and a complex series of reactions within the pretreatment solution. Any of these individual reactions can be disrupted if one of a number of influences (pH, temperature, electropotential gradients, etc.) is outside of a specified range.

In addition to these key solution parameters, the introduction or elimination of one component often can affect how a pretreatment is deposited and, correspondingly, how it performs.   For example, buildup of ferrous ion in a zinc phosphate bath can reach a critical level in which the crystalline zinc phosphate conversion coating is stopped and replaced by an amorphous iron phosphate coating.[15] In another example, the rates of deposition of chromate conversion coatings are often dependent on the presence of an accelerating agent such as an acid fluoride. This acid fluoride is believed to lower the activation energy during the conversion of the highly soluble hexavalent chromate ions to an inert and relatively insoluble trivalent chromium oxide layer. Depletion of the fluoride species can significantly alter the kinetics of the reaction resulting, in a much slower chromium oxide deposition.   It is important to note that the effect of any of these variables on the deposition of a viable or nonviable pretreatment layer is both substrate and coating dependent.

As alluded to above and discussed further below, testing revealed that the commercial Zircobond formulas, which have a history of successful use with automotive and industrial electrocoat formulations, were found to be problematic with CARC coatings over DOD substrates. It was quickly ascertained that the presence of one component, copper, was responsible for the poor performance.   Like the examples given above, it was clear that this component was behaving differently with the DoD substrates and / or coatings. It was also clear that a reliable, reproducible test protocol was needed to screen new variants of the zirconium pretreatment.

Although corrosion behavior cannot be guaranteed (*a priori*) from good adhesion results, the opposite is almost always true.   Poor adhesion will usually result in poor corrosion performance.   To determine if a coating system has good or poor adhesion, a number of tests have been used by coating formulators. Crosshatch Adhesion, Direct and Reverse Impact, Cylindrical and Conical Mandrel bends, and T-bends, are test protocols that have been used for years to determine how well a coating sticks to a pretreatment or a pretreatment to a substrate under conditions of a perpendicular pull-off, violent distortion(s), and controlled flex-stress. Although each of these tests can help to elucidate the relative "adhesive" strengths of the coating system (in a qualitative manner), one test, PATTI (Pneumatic Adhesion Tensile Testing Instrument) adhesion (ASTM D4541) can do it quantitatively. Testing conducted at PPG[16] prior to the work in this study has shown that the PATTI test can distinguish between coating systems with good adhesion to systems having borderline or poor adhesion. This work had been correlated with the Crosshatch Adhesion Test (ASTM D 3359) and showed that coating systems with PATTI values at or above 300 psi always yield crosshatch adhesion values of 5B and

usually resulted in good corrosion performance. Note that the reverse was not true. Crosshatch values of 5B were often obtained when PATTI results were less than 250 psi. These systems, however, often did poorly in corrosion tests.

With all of these considerations in mind, it was decided to use PATTI testing as the primary screening tool for the initial evaluation and later formula development to help determine which variants would have the best chance of successful specification testing. To help confirm the results seen in the PATTI tests, correlative testing with Crosshatch Adhesion and other standard tests were conducted at PPG and ARL as described below.

TECHNICAL APPROACH FOR DOD SUBSTRATES AND COATINGS

Zirconium-based pretreatments have been developed, and are currently being supplied to the automotive and general industrial markets. As part of this project, composition and process variations of this technology were compared for corrosion and adhesion on aluminum and steel substrates. Additionally, the pretreatment was tested with carbon fiber epoxy panels to determine if there was any detrimental effect. Commercial immersion and spray pretreatments were evaluated on DoD substrates and coated with water-borne and solvent-borne CARC systems. Experimental immersion and spray formulas were tested by ARL. These formulations consisted of the standard formulas, along with process modifications that previous testing had shown to increase the zirconium coating thickness and uniformity of the treatment film, or promoted the adhesion of the primer to the metal surface, or in general improved the corrosion performance in accelerated corrosion testing.

In order to provide a Spray-On/Rinse-Off zirconium pretreatment for depot and field use, the OEM spray and immersion formulas were modified with a thickener to hold the pretreatment on the part during the reaction and also with a copper salt to improve corrosion resistance. A Dried-In-Place zirconium pretreatment system was also developed with improved corrosion properties by adding either an organic-modified metal salt or by changing the source of zirconium.

MATERIALS AND APPLICATION METHODS
Substrates
1. Cold rolled steel (CRS) - 4" x 12"x.032" cleaned-only obtained from ACT Test Panels LLC, Hillsdale, MI
2. Aluminum 2024-T3 aluminum, 7075-T6 aluminum from California Metal & Supply, Inc. / Los Angeles, CA
3. Carbon fiber/epoxy panels, supplied by ARL.

Additives
Adhesion promoters:
- H_2SiF_6 (20-25% by weight) from Sigma-Aldrich
- H_2TiF_6 (60% by weight) from Sigma-Aldrich
- EPI-REZ 3540-WY-55 from Momentive Specialty Chemicals
- Silquest A-187 from Momentive Specialty Chemicals
- Silquest A-1120 from Momentive Specialty Chemicals

Corrosion Inhibitors:
- Organic acid-modified metal salt from Heubach
- Pyromellitic acid from Sigma-Aldrich
- Hydroxycinnamic acid from Sigma-Aldrich
- Sinapinic acid from Sigma-Aldrich

Etching promoters:
- NH_4HF_2 solid available Sigma-Aldrich, 10% w/w solution used to increase fluoride content

Metal Cleaners and Treatments
- Chemkleen 2010 from PPG Industries
- Chemkleen ALP from PPG Industries
- Ridoline® 298 from Henkel Corporation
- Alodine® 1200S from Henkel Corporation
- Turco® Deoxidizer 6-16 from the Henkel Corporation

Zirconium Oxide Film Promoters/Formers:
- Proprietary PPG copper additive
- $ZrO(NO_3)_2$ (35 weight % solution) from Sigma-Aldrich
- $H_2ZrO(SO_4)_2$ from Fisher Scientific

Rheology Modifiers:
- Laponite® OG from Southern Clay Products
- Laponite® XL21 from Southern Clay Products

Flash Rust Inhibitors:
- Sodium nitrite from BASF Corp.
- 2-Amino-2-methyl-1-propanol (AMP95) from ANGUS Chemical Company
- Drewgard® 795 SA (Sodium Nitrite) from Ashland Specialty Ingredients
- Ammonium benzoate from Fisher Scientific
- Sodium molybdate from Fisher Scientific
- FlashX®330 from Halox
- Raybo®60 No Rust (sodium nitrite, alkylamine) from **Raybo Chemical Company**
- Hold Tight®102 (amine) from HoldTight Solutions Inc.
- Nubirox®FR-20 (Dimethyl ethanolamine) from Nubiola USA Inc.

Cold rolled Steel or Aluminum Process (other than control Al)
1. Spray cleaning for 2 minutes with 1.25% Chemkleen 2010 /0.125% Chemkleen ALP from PPG industries
2. Rinsing 15 seconds by deionized water immersion
3. 20 seconds deionized water spray
4. Application of pretreatment

5. 20 second deionized water spray
6. 2 minutes hot air drier

Aluminum Control Process
Alodine® 1200S chromium pretreatment was applied to aluminum as follows:
1. Ridoline® 298 cleaner for 2 minutes at130°F
2. Tap water immersion 1 minute at room temperature
3. Tap water spray 1 minute
4. Turco® Deoxidizer 6-16 1 minute
5. Tap water immersion at room temperature 1 minute
6. Alodine® 1200S pretreatment immersion 2.5 minutes
7. 1 minute deionized water rinse

Spray-On/Rinse-Off pretreatment was applied by spraying the pretreatment with a hand spray bottle and allowing the treatment to dry at room temperature and humidity, followed by a deionized water rinse and air drying.

The Dried-In-Place pretreatment was applied by spraying with a hand spray bottle, followed by allowing the treatment to air dry under ambient conditions.

RESULTS AND DISCUSSION

1. OEM Pretreatment Development

1.1 Immersion Zirconium Pretreatment

1.1.1 Compatibility Testing of OEM Product with DoD Substrates

The compatibility of OEM immersion zirconium pretreatment with DoD substrates was determined in conjunction with Pauline Smith of ARL. It was determined that the initial set of DoD relevant substrates would include: cold-rolled steel (CRS), 2024-T3 aluminum, 7075-T6 aluminum, and a graphite/epoxy composite.

An initial set of panels was pretreated with two OEM immersion zirconium pretreatments which consisted of Zircobond4200 and Zircobond4200 without the copper salt. Panels of CRS, 2024-T3 aluminum, 7075-T6 aluminum, and graphite/epoxy composite were exposed to the OEM formulas. CRS, 2024-T3 aluminum, and 7075-T6 aluminum samples each exhibited an integral coating that varied in color from white to blue/black. Panel color was dependent on the substrate and whether (or not) the treatment contained copper (see **Figure 6**; Note that 2024-T3 samples were similar to 7075-T3). In the absence of copper, the CRS and aluminum samples had a coating that was white and heterogeneous in appearance. With the copper present in the coating, the aluminum and CRS coatings were white to blue/black in appearance and homogenous in appearance. The zirconium deposition was confirmed by XRF spectroscopy. Coating weights and zirconium thickness were also determined by XRF (for a full discussion of methodology of zirconium pretreatment film measurement see ASTM D7639). Coating thickness

values are given in **Table 1**. Based on these results, it was determined that all DoD substrates of interest may be coated with zirconium pretreatment with the exception of the graphite/epoxy composite. However, this substrate was included to determine if the zirconium pretreatment had any detrimental effects on the composite. Upon coating no change in appearance was observed. Panels were sent to ARL for evaluation. Evaluation by ARL determined that there were no detrimental effects to the composite.
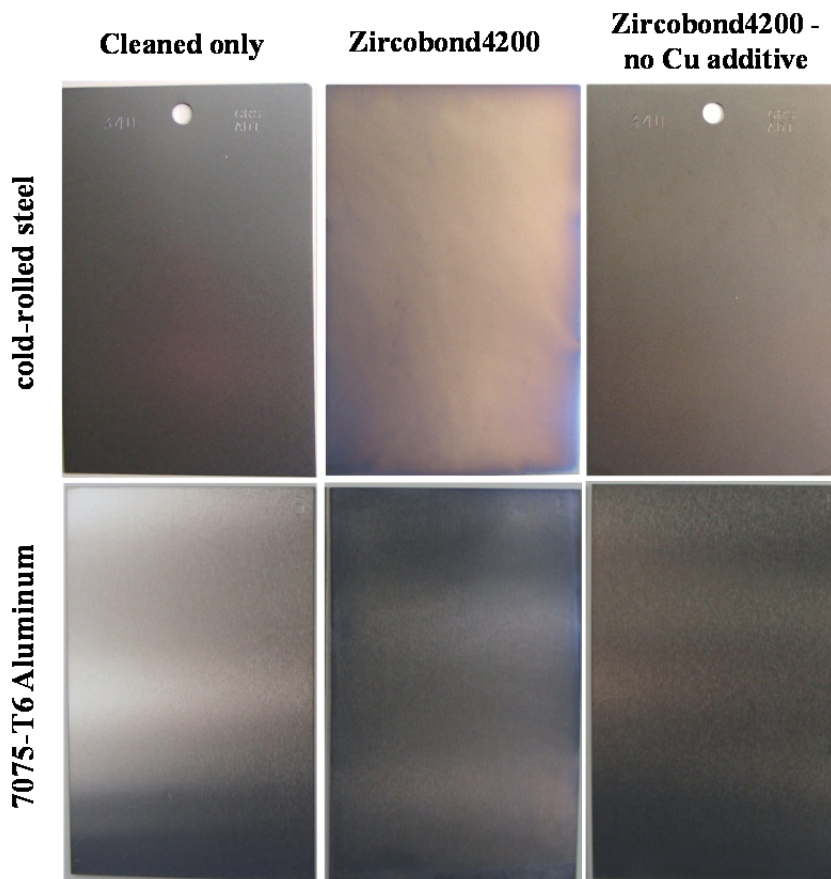
Figure 6. Appearance of Aluminum and CRS treated with Immersion Zirconium Pretreatment

	CRS	7075-T6
	thickness, nm	thickness, nm
Zircobond4200	85	46
Zircobond4200 Cu additive	73	37

Table 1. Zirconium thickness.

A benchmark study was then conducted to determine how OEM immersion zirconium

pretreatments perform in corrosion under primers designed for the CARC system. Zircobond4200 and Zircobond4200 without copper were tested under MIL-DTL-53022 (solvent-borne) or MIL-DTL-53030 (water-reducible) epoxy primers on CRS using PATTI adhesion, 20 cycles GMW14872, and 400 hours ASTM B117 versus tricationic zinc phosphate and chrome (VI) wash primer controls. PATTI adhesion showed comparable performance for zinc phosphate and Zircobond4200 with no copper. A modest decrease in adhesion was noted for Zircobond4200 and the chrome (VI) system (See **Figure 7a**). After 16 hours at 140°F and condensing humidity, the performance on the zinc phosphate and Zircobond4200 without copper was again equivalent. The Zircobond4200 system, however, showed near total failure under these conditions (See **Figure 7b**). Similar results were observed on 6061-T6 Al. However, overall pull-off tensile strength values were less than 500 psi for all samples (a 300 psi pull-off adhesion value is roughly equal to a 5B per ASTM D 3359 crosshatch evaluation).
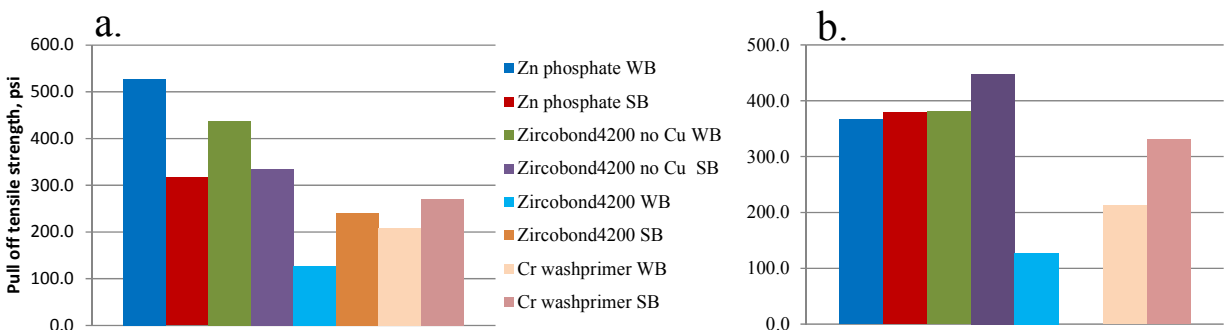
Figure 7. PATTI adhesion testing with various pretreatments with waterborne (WB) and solventborne (SB) primer systems. Samples were tested at ambient conditions (a) and after 16 hours at 140°F and condensing humidity (b).

The pretreatment systems were also evaluated using ASTM B117 (400 hours) and GMW14872 (20 cycles). Performance evaluation is carried out by preparing 4x6 inch treated and primed panels, subjecting the panels to the specified environmental conditions for the specified time, after which they are examined for corrosion size, location and density as described in Federal Specifications TT-C-490, MIL-DTL-53022 (solvent-borne CARC primer), and MIL-DTL53030 (water-borne CARC primer). Unless otherwise noted, the creepage or undercutting of the paint film (known as "scribe creep") is reported as the mean *overall width* of the corrosion zone. The specifications call for undercutting of the paint film by no more than 3 millimeters (1/8 inch) mean creepage *from the scribe*.

In these tests, it was apparent that the waterborne systems had systematic problems with the paint due to near total failure over all pretreatments including controls. Therefore only the solvent borne testing was considered valid. In ASTM B117, Zircobond4200 with no copper performed similar to zinc phosphate (See **Figure 8a**). However, in GMW14872, Zircobond4200 with no copper performed similar to the chrome (VI) wash primer, but tricationic zinc phosphate outperformed all systems (See **Figure 8a**). This experiment brought to light two observations for the OEM immersion pretreatment systems. 1) Systems containing copper performed poorly in exposed adhesion testing and corrosion testing. 2) In GMW14872, even the best performing

system, Zircobond4200 with no copper, was similar to the wash primer, but not equal to zinc phosphate control.
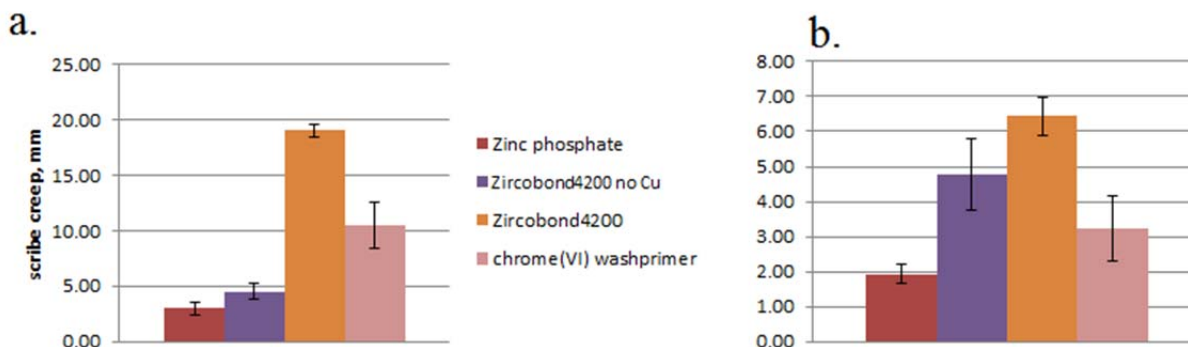
Figure 8. Four hundred hours neutral salt spray (a) and 20 cycles GMW14872 (b) of various pretreatments with a solvent borne (SB) primer system.

An in-depth investigation was conducted to determine the role of the copper additive in performance loss**.** This information was used to reformulate the zirconium-based pretreatments for use with DoD coatings systems. Zirconium pretreatments containing copper were again evaluated using PATTI adhesion testing. After exposure to 16 hour 140°F with condensing humidity, samples containing copper had a nearly complete loss of adhesion (pull-off tensile strength values <100 psi), while samples without copper had pull-off tensile strength values >500 psi. This work agreed well with earlier work which suggested that copper caused the OEM formula Zircobond4200 to perform poorly.

This phenomenon was studied by looking at the effect of copper on paint cure. Free films of the solvent-borne CARC primer were generated with 0, 30, 300, and 2500 ppm copper in the film. Thirty ppm of copper represents a large amount of migration from the coated panel into the primer film (the system was also tested at 10 and 100 times that level). The two samples had comparable cure and T_g (57°C), as measured by dynamic mechanical analysis. Results from these experiments suggested that the poor performance resulted from the interfacial interaction of copper with the amine catalyzed epoxy primer used in the CARC system, and not from cure effects induced by copper. This is exemplified in the loss of adhesion under the exposed PATTI (16 hours, 140°F**,** with condensing humidity) conditions. This initial experiment highlights the importance of pretreatment formulation to the performance of the subsequent coating system.

The second observation from the initial experiment was that the best performing OEM immersion zirconium system, Zircobond4200 without copper, performed similar to zinc phosphate and better than chrome (VI) wash primer after 400 hours salt spray. In GMW14872 (20 cycles) the system performed equal to chrome (VI) wash primer and modestly lower than zinc phosphate in GMW14872 (20 cycles). Although these results suggest that the best OEM immersion zirconium pretreatment formulation may perform similar to chrome (VI) wash primers in accelerated corrosion testing, the system would need to be further modified to perform equal to zinc phosphate in cyclic corrosion.

1.1.2 Compatibility Testing of OEM Product with DoD Paint Systems

Results from substrate compatibility testing suggested that Zircobond4200 (with or without copper) would require some modification prior to submission of coated panels for specification testing at ARL. During these initial experiments, performers from ARL and PPG met to determine the most efficient means of testing formulas for performance. In an effort to explore multiple formulations in a timely fashion, testing was broken up into 2 stages. Stage 1 testing included adhesion (ASTM D3359), water resistance (ASTM D1308) and JP8 resistance over cold rolled steel substrates. Stage 2 test included an expansion of substrates and salt fog (ASTM B117) and cyclic corrosion testing (GMW 14872). It was decided to exclude top coats from testing to allow for a thorough analysis of the pretreatment effect on the primer.

CRS, 7075-T6, and 2024-T3 panels were pretreated with Zircobond4200 with and without copper, and then submitted to ARL to be painted with solvent and water-reducible CARC coating systems. The panels were then tested according to ASTM D3359 (adhesion testing), ASTM D1308 (water-immersion testing), and by JP8 fluid immersion (adhesion testing). Zircobond4200 without copper passed all adhesion testing; however, the standard Zircobond4200 (with copper) failed (see **Tables 2 and 3**). Again, these results from ARL agreed well with PPG's internal testing which suggested that copper hurt performance under the CARC coating system. Feedback from ARL suggested that even though the Zircobond4200 system without copper passed all adhesion testing, some panels were marginal. Based on this feedback, improvements in adhesion were sought.

	Test	Standard	Zinc phosphate	Zircobond4200	Zircobond4200 no Cu additive	Chrome(VI) wash primer
Cold-rolled steel	Wet/dry adhesion	ASTM D3359	4B	3B	5B	5B
	Water immersion	ASTM D1308	3B	2B	4B	4B
	JP8 fluid immersion	-	4B	3B	5B	5B
A2024-T3	Wet/dry adhesion	ASTM D3359	-	3B	5B	5B
	Water immersion	ASTM D1308	-	2B	5B	5B
	JP8 fluid immersion	-	-	4B	5B	5B
A7075-T6	Wet/dry adhesion	ASTM D3359	-	2B	5B	5B
	Water immersion	ASTM D1308	-	3B	4B	5B
	JP8 fluid immersion	-	-	3B	5B	5B

Table 2. Adhesion of solvent-borne CARC coating system (Ratings of 4B and 5B are considered passing values).

Test	Standard	Zinc phosphate	Zircobond4200	Zircobond4200 no Cu additive	Chrome(VI) wash primer
Wet/dry adhesion	ASTM D3359	5B	2B	4B	4B
Water immersion	ASTM D1308	4B	1B	4B	4B
JP8 fluid immersion	-	5B	1B	4B	4B
Wet/dry adhesion	ASTM D3359	-	2B	5B	5B
Water immersion	ASTM D1308	-	1B	5B	4B
JP8 fluid immersion	-	-	1B	5B	5B
Wet/dry adhesion	ASTM D3359	-	0B	4B	5B
Water immersion	ASTM D1308	-	0B	4B	4B
JP8 fluid immersion	-	-	3B	4B	5B

Table 3. Adhesion of solvent-borne CARC coating system (Ratings of 4B and 5B were considered passing values).

Prior to the follow-up submission to ARL, two studies were conducted to determine 1) if typical modifications such as pH or post-processing modifications would improve performance and 2) if the addition of adhesion promoters would improve the adhesion and, in turn, corrosion, of the zirconium systems. Also, it should be noted that all subsequent experiments in Tasks 1 and 2 at PPG were conducted with solvent borne (MIL-DTL-53022) approved primers due to inconsistencies in performance with the water reducible primer(s). All systems in Tasks 1 and 2 which performed well in the screening testing with solvent borne primers were submitted to ARL for full testing with both solvent and water borne primer systems.

Work was conducted to identify factors, such as pH, application time, and/or level of copper, which would improve the corrosion performance of the baseline formula of Zircobond4200. While typical application takes place at a pH of 4.7, at a pH of 4.2 improved performance was observed in 500 hour ASTM B117 at longer application times (see **Figure 9**). However, at this lower pH, the hexafluorozirconic acid complex is too soluble and deposition, and subsequently performance, is negatively impacted. Finally, the major observation of this study was further confirmation that immersion zirconium pretreatments with copper perform poorer than systems without copper (see **Figure 9**). Best performance was observed at pH 4.2 and 6 minute application time with no copper or at pH 4.7 with no copper.
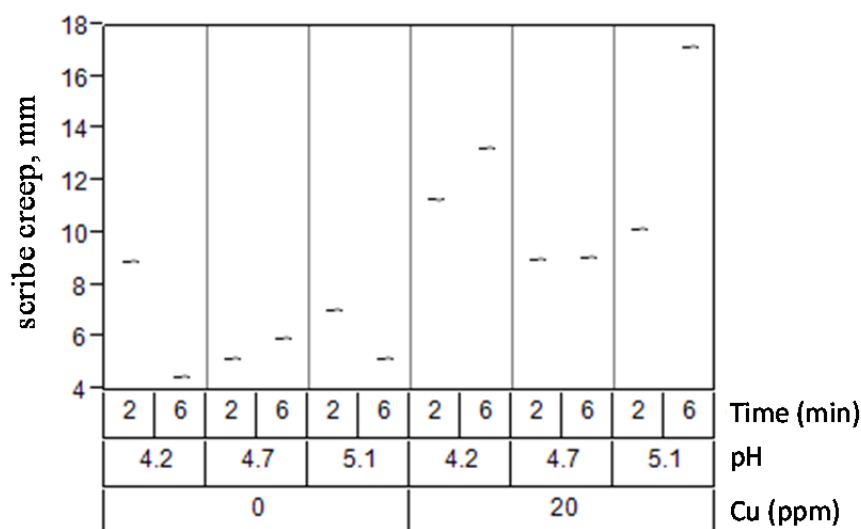
Figure 9. Five hundred hours neutral salt spray at various conditions. Conditions tested were immersion application time, pH and Cu additive content.

In addition to modifying bath parameters, adhesion promoting compounds (see above) were evaluated for improvement of corrosion performance prior to the first submission to ARL. Additions of tetraethyl orthosilicate, Silquest A-187, or H_2SiF_6 (all at 18 and 61 ppm of silicon so that zirconium + silicon in ppm = 175) were evaluated as additives to improve adhesion and subsequently corrosion. These samples were evaluated for adhesion using PATTI. In PATTI testing, the Silquest A-187 (18 ppm of Si) and H_2SiF_6 both showed improved adhesion (however the overall pull-off strengths for all samples were low) (see **Figure 10**). These samples were also evaluated in 20 cycles of GMW14872. In this test the results agreed well with the PATTI, however with Silquest A-187 the results were mixed (low levels good for corrosion and higher levels were good for PATTI adhesion, but not *vice versa*) (see **Figure 11**). Performance of H_2SiF_6 modified Zircobond4200 (no copper) was sufficient for further evaluation at ARL.
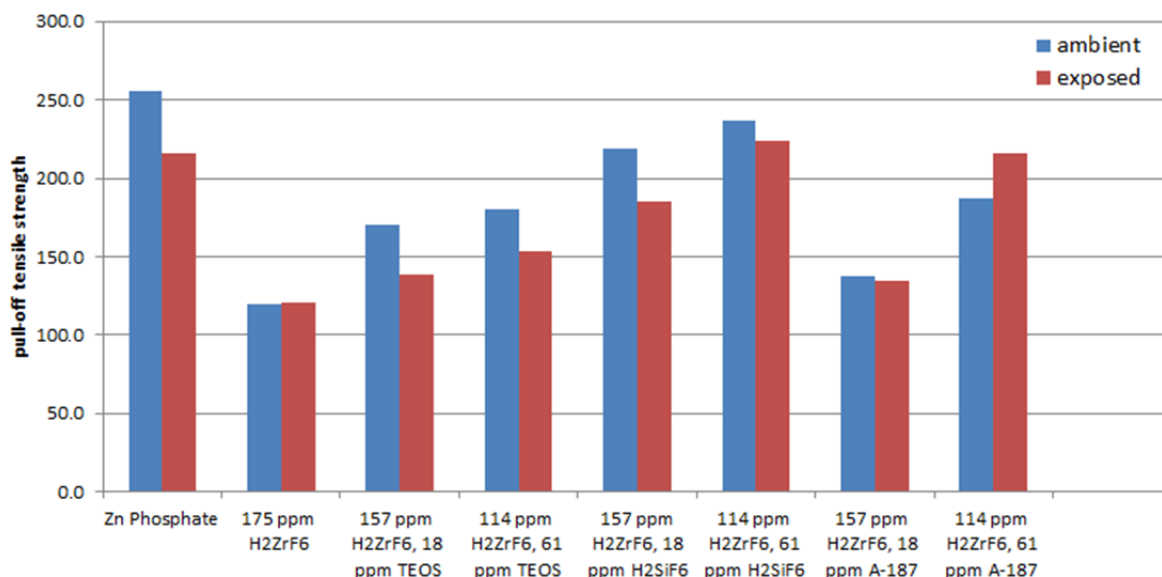
Figure 10. PATTI adhesion testing with various pretreatments with solventborne primer systems. Samples were tested at ambient conditions and exposed conditions (16 hours at 140°F and condensing humidity).
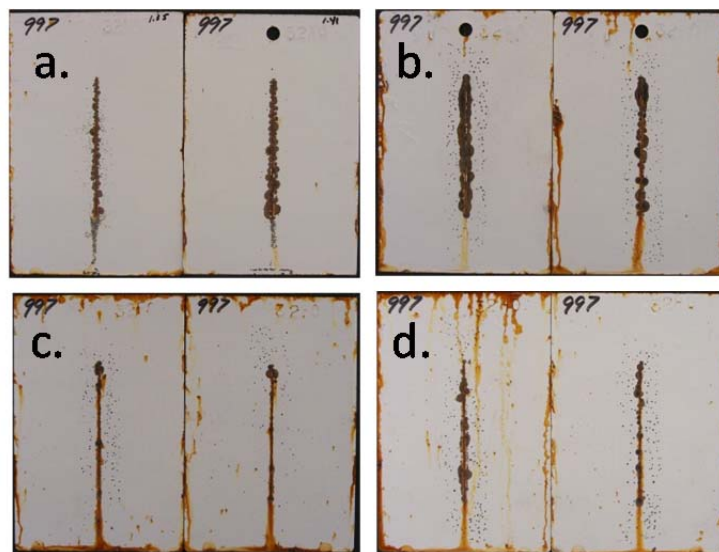
Figure 11. Five hundred hours neutral salt spray. Panel (a) is tricationic zinc phosphate. Panel (b) is Zircobond4200 no Cu additive. Panel (c) is the same as (b) with added H2SiF6 (20 ppm as Si). Panel (d) is the same as (b) with Silquest A-187 (5 ppm as Si).

Therefore data from these two experiments led to the design of a set of panels for submission to ARL for phase 1 adhesion testing. The submitted systems (all were without copper) included Zircobond4200 pH 4.2 with a 6 minute application, pH 4.7 with a 2 minute application, 20 ppm addition of H_2SiF_6, an experimental epoxy resin additive (stable epoxy to replace the Silquest A-187), and pH 4.7 with a 2 minute application but with a post-treatment bake at 350°F for 25 minutes after zirconium application (this had shown improved performance in prior testing).

Samples for ARL experiment 1 were pretreated at PPG and sent to ARL for primer application and adhesion testing. Upon arrival, it was noted that some of the CRS panels had flash rusting. To mitigate this, a second full set of panels was sent to ARL (experiment 2) in VCI (Volatile Corrosion Inhibiting) Kraft paper. Upon arrival at ARL, the panels were individually inspected. There was no sign of corrosion or damage on the panels during the inspection. All of these panels were determined to be suitable for testing.

Samples were successfully coated with either MIL-DTL-53022 solvent-based epoxy primer or MIL-DTL-53030, water-reducible epoxy primer, followed by top coating with MIL-DTL-64159 Type II.

After stage 1 testing, ARL was prepared to move to stage 2 corrosion testing with the Zircobond4200 samples with a 20 ppm addition of H_2SiF_6 and the sample at pH 4.7 with a 2 minute application, but with a post-treatment bake at 350°F for 25 minutes after zirconium application (see **Table 4**).

Pretreatment	Primer System	ASTM D3359	Water	JP8
tricationic zinc phosphate	MIL-DTL-53022	4B	5B	4B
tricationic zinc phosphate	MIL-DTL-53030	5B	4B	4B
chrome (VI) wash primer	MIL-DTL-53022	4B	4B	4B
Chrome (clean only)	MIL-DTL-53030	5B	5B	4B
pH 4.2, 6 min	MIL-DTL-53022	3B	3B	3B
pH 4.2, 6 min	MIL-DTL-53030	2B	1B*	2B
pH 4.7, 2 min	MIL-DTL-53022	4B	4B	4B
pH 4.7, 2 min	MIL-DTL-53030	5B	3B	4B
pH 4.7, 2 min, 350 F 25' cure	MIL-DTL-53022	4B	4B	4B
pH 4.7, 2 min, 350 F 25' cure	MIL-DTL-53030	5B	5B	4B
pH 4.7, 2 min, 0.25 w% EPI-REZ 3540-WY-55	MIL-DTL-53022	4B	4B	4B
pH 4.7, 2 min, 0.25 w% EPI-REZ 3540-WY-55	MIL-DTL-53030	5B	3B	4B
pH 4.7, 2 min, 20 ppm Si (from H_2SiF_6)	MIL-DTL-53022	4B	4B	4B
pH 4.7, 2 min, 20 ppm Si (from H_2SiF_6)	MIL-DTL-53030	5B	5B	4B
* Panel blistered in the emersed area. Rust developed in the blisters.				

Table 4. Adhesion performance of immersion prototype pretreatments.

A follow-up set of panels was shipped to ARL for stage 2 corrosion testing (and adhesion testing on Al and composite substrates) (shown below in **Table 6**). Samples were coated with primer only, and submitted for ASTM B117 and GMW14872 testing. CRS samples passed the specified 336 hours in ASTM B117 and 20 cycles in GMW14872. The experimental samples were comparable to tricationic phosphate and DOD-P-15328 wash primer. Samples performed well in 1008 hour (6 rating per ASTM D 1654) ASTM B117, however not as well as the controls. The system was also similar to the controls in 40 cycles GMW14872.

In this study, aluminum was also tested. Samples of 2024-T3 and 7075-T6 aluminum were tested with the two variations of existing zirconium-based immersion pretreatments. The aluminum samples were coated with no visible surface defects. Samples were successfully coated with either MIL-DTL-53022 solvent-based epoxy primer or MIL-DTL-53030, water-reducible epoxy primer. Samples coated with MIL-DTL-53030 and samples coated with MIL-DTL-53022 were top coated with MIL-DTL-64159 Type II. The samples were then tested according to ASTM D3359 (adhesion testing), ASTM D 1308 (water-immersion testing), and by JP8 fluid immersion (adhesion testing). Panels pretreated using the existing zirconium-based formula *without* copper performed equal to, or better than, zinc phosphate and chrome wash primer controls in the aforementioned tests. Corrosion results showed that the Al samples also performed well in 1008 hour (6 rating per ASTM D 1654) ASTM B117, however again not as well as the controls. The system was also similar to the controls in 40 cycles GMW14872.

From these studies it was apparent that a modified Zircobond4200 pretreatment with no copper additive could perform to the minimum standard of tests outlined in MIL-DTL-53022 and MIL-DTL-53030. However, it was also apparent that the tested systems need to be improved in anticipation of more stringent corrosion testing. In addition, a discussion with ARL around the viability of post-processing modifications using heat suggested that this approach may not be possible at a typical depot site. Further work was required to improve the corrosion performance of the Zircobond4200 with no added post-processing steps.

1.1.3   Reformulation and Testing of Immersion Zirconium Pretreatment

While the charge for this task was to modify the commercial immersion formulas for better performance in specification testing, some of that work was conducted as part of the previous task. Adhesion-promoting compounds were added to the formulation for improved corrosion performance. H_2SiF_6 was the most promising candidate for further investigation in this task. Additionally, a post-processing bake provided the best performance. However this process is not optimal for application in a DoD depot. This task, therefore, centered on learning why the post-processing step or the inclusion of H_2SiF_6 provided better performance. Additionally, this task included the evaluation of processing parameters for best performance in DoD applications.

During the execution of this project, it was noted that the commercial automotive OEM immersion zirconium pretreatments (albeit with electrodeposited primers) operated well at levels of free fluoride (F^-) higher than the initial charge. While an automotive tank is charged initially with the bath components, the progress of deposition leads to an increase in F^- content (see **Equation 1**). An operating zirconium bath in the field functions well in a range between 50 and 100 ppm, even though the initial bath is formulated at 25 ppm F^-. This observation from the field lead to an experiment to test levels of F^- akin to field baths currently operating, and compare them to the best performing prototype Zircobond4200 without copper and or H_2SiF_6 (10-40 ppm by Si).

$$H_2ZrF_6 + 2OH^- \rightleftharpoons ZrO_2(s) + 6F^- + 2H_2$$
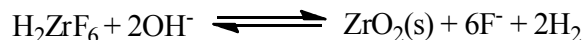
Equation 1. Metathesis reaction of fluorozirconic acid in presence of hydroxide

An experiment was conducted to compare samples coated with Zircobond4200 at the following conditions: 0 and 20 ppm of copper; 0, 10 and 40 ppm of H_2SiF_6; and 25, 75, and 200 ppm of F^-. The purpose of this experiment was to determine if the improvement gained from the addition of the H_2SiF_6 was the result of the additive or the additional F^- brought into the system. Samples were coated with solvent-borne CARC primer (MIL-DTL-53022B) and subjected to 500 hours ASTM B117 testing. For *all variables tested*, the systems without copper outperformed the comparable Zircobond4200 systems (with copper). The increased F^- system with, or without the H_2SiF_6, performed well. This indicated that the H_2SiF_6 was not necessary for improved results (see **Figure 12**). That is, a higher level of F^- in Zircobond4200 without copper could perform well without the Si additive. Therefore, further submissions to ARL for testing (which are mentioned below) focused on a Zircobond4200 variation without copper at an elevated level of F^- in the bath. This has the added benefit of providing a fluoride condition that will be easier to maintain in the field. This is an important point because when the F^- content is too high, zirconium-based pretreatment films are thin resulting in poorer performance. This is exemplified in **Equation 1** which describes the deposition process, and resulting F^- generation. As you increase the products on the right side of **Equation 1**, the reaction equilibrium is driven to the left (or to reactants). The higher F^- content allows the hexafluorozirconic acid to be too soluble, thus retarding deposition. This is controlled by placing limits on the F^- content of the system, and also by controlling the bath pH. The bath pH also plays a role, a reduced role compared to F^-, in causing the hexafluorozirconic acid complex to be too soluble. When pH is decreased, hexafluorometallates become more soluble.

The second target of this task was to better understand the improved corrosion performance of zirconium pretreatments after heat treatment. While this approach is not optimum for DoD application, work was conducted to test whether the corrosion improvement observed might be made by chemical means. The deposition of zirconium oxides from hexafluorozirconates or zirconium alkoxides results in similar coatings.[17] The coatings that result are therefore not simply a zirconium oxide, but a mixture of zirconium oxides, hydroxides, and fluorides.   In sol-gel chemistry, the applied coating must progress through condensation reactions to transform from a mixed oxide/hydroxide state to an oxide state.[18] This reaction is promoted by two methods: 1) heating the surface and driving the condensed water out and 2) using acid or base to catalyze the reaction. As noted above, the addition of heat to the zirconium coatings has improved the corrosion performance. Work was conducted to determine if the condensation reaction might be promoted by acid or base post rinsing of the zirconium surface.
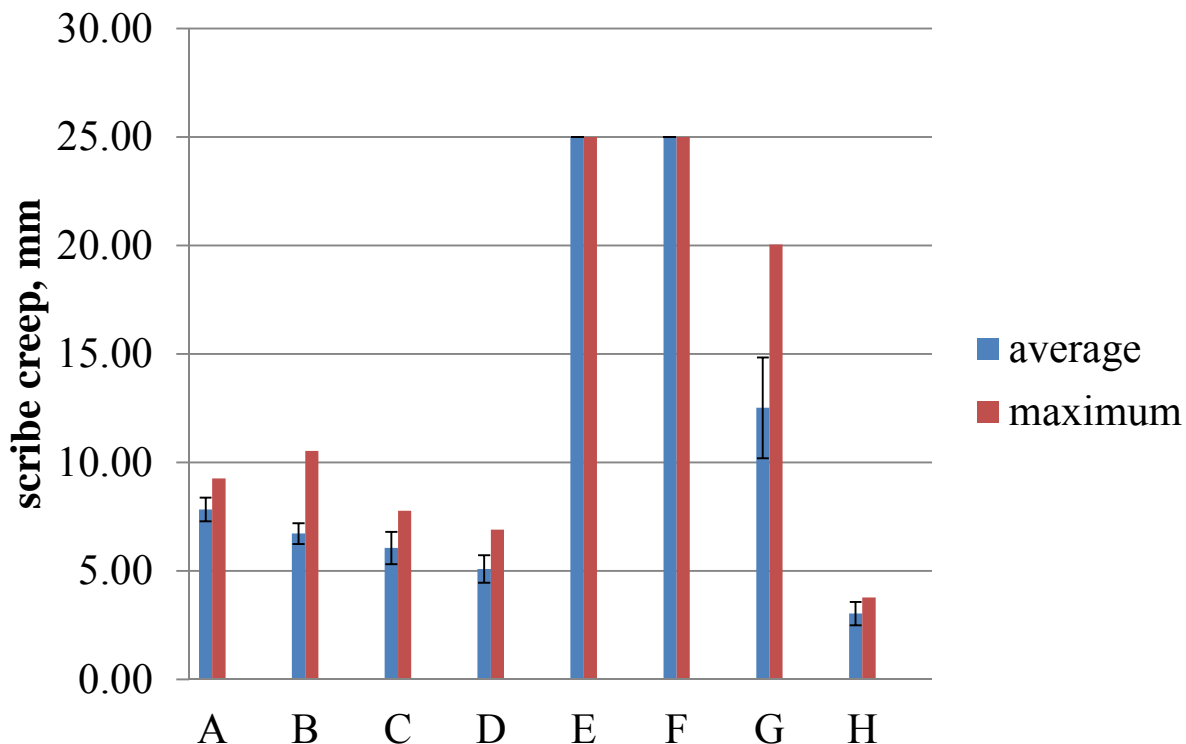
Label	Pretreatment
A	Zircobond4200 + 10 ppm H_2SiF_6 + 0 ppm of Metal A, 75 ppm of F-
B	Zircobond4200 + 40 ppm H_2SiF_6 + 0 ppm of Metal A, 75 ppm of F-
C	Zircobond4200 + 0 ppm of Cu additive, 75 ppm of F-
D	Zircobond4200 + 0 ppm of Cu additive, 200 ppm of F-
E	Zircobond4200 + 20 ppm of Cu additive, 75 ppm of F-
F	Zircobond4200 + 20 ppm of Cu additive, 200 ppm of F-
G	Zircobond4200 + 20 ppm of Cu additive, 25 ppm of F-
H	zinc phosphate

Figure 12. Five hundred hours neutral salt spray

Zircobond4200 (no copper, 80 ppm F-) samples were prepared and post treated under several conditions: with a 350°F for 20 minutes heat treatment; a pH 12 (NaOH) for 1 minute alkaline treatment, or with no post treatment (acid rinse was not run due to the dissolution of zirconium when exposed to acid conditions). These samples were evaluated by SEM to determine if driving the condensation leads to coating shrinkage and cracking. Coating shrinkage and cracking is apparent from the SEM images in **Figure 13**. Both post treatment with heat and alkaline solution drives condensation, and consequently, leads to film cracking. Each of the two post-treated films peeled from the substrate to the point where the bare substrate was visible. Due to feedback from ARL that a heat post-treated pretreatment is not optimum for DoD

applications and the observation of a compromised film, no further work in post treatments was deemed useful. However, it must be noted that even though the heat-treated systems had compromised films, corrosion was improved. Further work on this finding would be of direct interest for future zirconium pretreatment technologies.
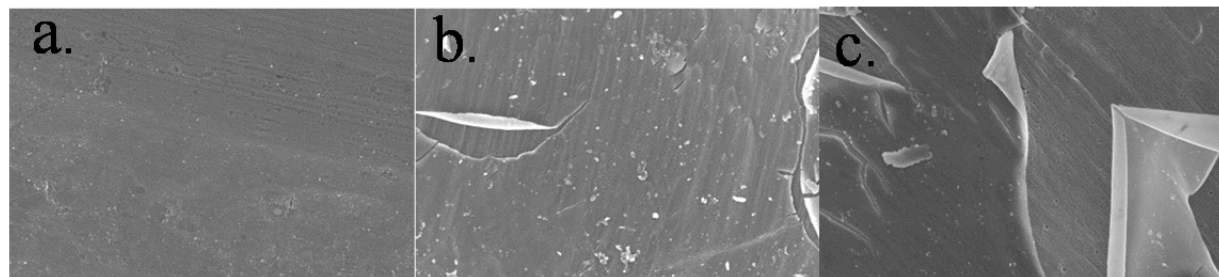
Figure 13. SEM images of zirconium pretreatment on CRS at 10,000 times magnification. (a) SEM of prototype immersion zirconium. (b) SEM of prototype immersion zirconium with 350 °F bake for 20 minutes. (c) SEM of prototype immersion zirconium pH 12 (NaOH) post rinse 1 minute.

While not pursued further, additional work was conducted to improve the performance of Zircobond4200 by increasing the deposition of the zirconium oxide film without the use of copper. This was done by addition of a second zirconium source, $ZrO(NO_3)_2$, which does not provide additional F^-. Additionally, formulating with $ZrO(NO_3)_2$ allows for the use of corrosion inhibitive metal salts traditionally insoluble in the presence of free fluoride.[19]

$ZrO(NO_3)_2$ was evaluated for application of a zirconium oxide film without hexaflurozirconic acid. Spray and immersion of cold-rolled steel panels in the zirconium pretreatment resulted in a color change and apparent film formation. Scanning electron microscopy was used to evaluate the coating morphology. Micrographs (see Figure 14) suggested that use of the new starting material resulted in a different coating morphology when compared to the commercial zirconium pretreatments. Additionally, these new pretreatments are formulated so that they are compatible with corrosion inhibitive metal salts of cerium, yttrium, and praseodymium, traditionally insoluble in the presence of free fluoride. Formulations with the aforementioned metal salts also resulted in visually distinct coatings. X-ray fluorescence (XRF) was used to confirm the presence of the metals integrated into the coating. Additionally, the XRF demonstrated that the alternative zirconium material yielded an increase of deposited zirconium (presumably oxide) film when used as an additive to Zircobond4200 (See Table 5). Note that the kilocounts per second measurement is related directly to the amount of deposited zirconium). The new systems were evaluated under the amine-catalyzed epoxy primer (MIL-DTL-53022) in 20 cycles of GM9511P. In this screening test, several of the novel zirconium formulas (with varied operating parameters) outperformed commercial zirconium pretreatments (~4 mm vs. 6-8 mm of scribe creep). Zinc phosphate performed equal to the new zirconium pretreatments. These samples, however, were also evaluated by GMW14872 and ASTM B117. In these tests, the corrosion performance was not greatly improved (even with the higher zirconium content on the panels). Due to the lack of performance improvement in the DoD required tests, and the cost of the inhibitors investigated, no further work was conducted with the alternative zirconium source.
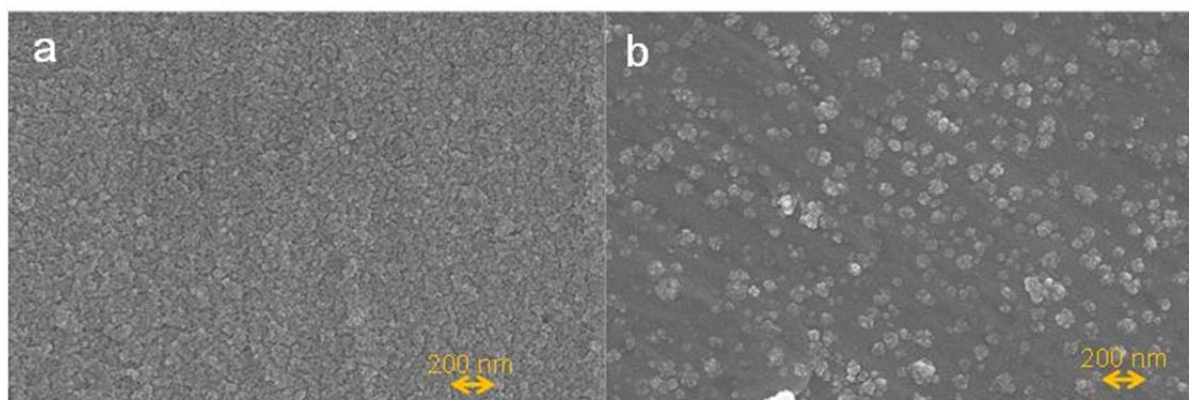
Figure 14. SEM of (a) immersion ZrO(NO$_3$)$_2$ pretreatment and (b) Zircobond4200 immersion pretreatment on CRS at 10,000 times magnification

	Standard OEM Immersion Zr Pretreatment	Standard OEM Immersion Zr Pretreatment + novel Zr additive
Zirconium Intensity from XRF (kilocounts/s)	28.4	36.3

Table 5. XRF measurement of zirconium intensity.

Several approaches were taken to improve the Zircobond4200 formula for performance in DoD testing over DoD specific substrates. Adhesion and deposition promoters were tested. The best performing system in internal testing is similar to the current commercial immersion Zircobond4200 system, only at higher levels of free fluoride and without copper. Samples of this system which demonstrated good performance in local testing were therefore submitted to ARL for full specification testing. A set of panels was prepared which tested the best performing Zircobond4200 system, at higher levels of free fluoride and no copper. This sample was compared to tricationic zinc phosphate and chrome (VI) wash primer.

Samples of CRS, 2024-T3, and 7075-T6 that were tested and coated had no visible surface defects. Samples were successfully coated with either MIL-DTL-53022 solvent-based epoxy primer or MIL-DTL-53030, water-reducible epoxy primer. These systems were tested in 20 and 40 cycles of GMW14872 and 336 and 1008 hours of ASTM B117. Zircobond4200 without copper additive and 80 ppm of free fluoride performed well in 336 hours ASTM B117 and 20 and 40 cycles GMW14872 with both the MIL-DTL-53022 and MIL-DTL-53030 primer systems on all three substrates. In 1008 hours of ASTM B117, the prototype system was given a

passing rating; however, it did not perform equal to tricationic zinc phosphate control (results given in **Table 6**).

	ASTM B117		GMW14872	
	336 hours	1008 hours	20 cycles	40 cycles
Tricationic zinc phosphate	Pass	Pass	Pass	Pass
Chrome(IV) wash primer	Pass	Pass	Pass	Pass
Zircobond4200	Marginal	Fail	Marginal	Fail
Zircobond4200 no Cu and 80 ppm of F⁻	Pass	Pass	Pass	Pass

Table 6. Performance of the immersion formula in corrosion testing.

The passing ratings of the prototype system prompted a request from ARL to put samples in long-term outdoor testing. ARL requested, and PPG supplied, a set of CRS and aluminum (2024-T3 and 7075-T6) panels pretreated under optimal operating experimental conditions. All panels were then top coated with MIL-DTL-64159 type II, and are being tested to failure. Analysis on the panels will include corrosion ratings, color, and gloss. Samples were submitted for outdoor exposure at NASA's Cape Canaveral beach corrosion site. This testing will be monitored as part of the WP-201318 ESTCP program.

1.1.4   Immersion Turnover Study

A turnover study was conducted with the immersion prototype formulation. Two hundred 4x12" panels were run through a 1 gallon bath of the prototype immersion formula while controlling pH and free fluoride (Zircobond4200 replenisher, ZB4200DR, was used to reduce pH). All work was conducted at pH 4.7, 80°C. This study represents ~2 weeks in a production line running a moderate schedule equivalent to two daily shifts for five days a week.

It was noted that replenishment using ZB4200DR over this range was not sufficient to maintain zirconium content (See **Figure 15**). The total fluoride also tended to drift downward. This observation further suggests the there is deposition of F⁻, in addition to oxides and hydroxides in the film (fluoride is also observed in the film by XPS).   Finally, with this replenishment method, the iron content rises. Thus, a replenisher system will need to be designed to better maintain bath conditions in the prototype immersion system.
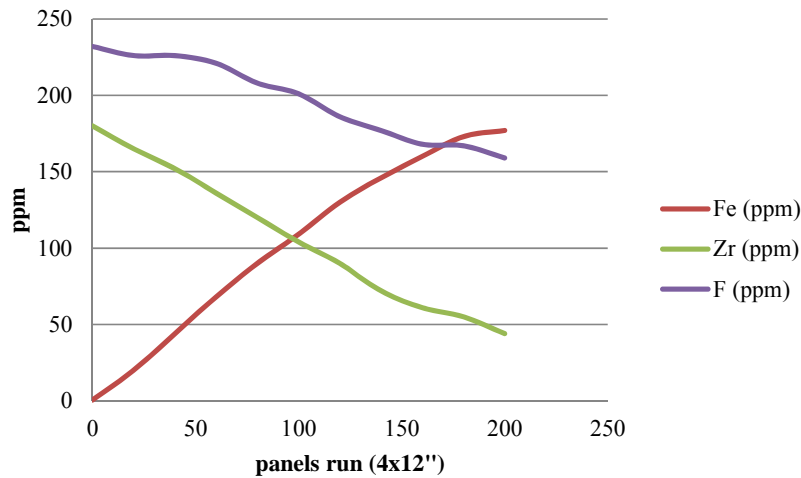
Figure 15. Zircobond4200 immersion prototype followed by ICP and F⁻ ion selective electrode (F is total fluoride not free fluoride).

This throughput investigation highlights the robustness of the immersion zirconium pretreatment systems even at suppressed zirconium levels. Samples were taken every 20 (prior to bath adjustment) and 21 (after adjustment) panels, coated with the solvent-borne primer system (MIL-DTL-53022) and tested in 20 cycles of GMW14872, which indicated that corrosion performance was maintained from the beginning to the end of the study. **(See Figure 16).** This suggests that the level of zirconium needed is lower than initially formulated, but ensures that the bath will operate even after a large number of panels are coated. As long as the free fluoride and pH are maintained, the system performs well in corrosion testing. Letting the free fluoride get too high, or letting the pH get too low, will lead to more soluble hexafluorozirconic acid compounds and coatings which may be too thin. However, for long-term bath operation, the replenishment system must be adjusted.
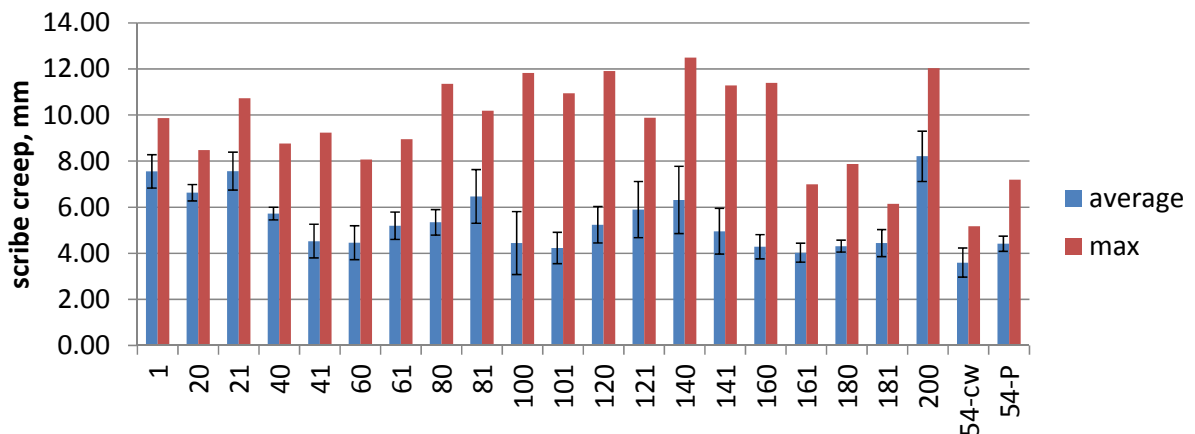
Figure 16. Zircobond4200 immersion prototype tested in 20 cycles of GMW14872 after a given number of panels were run through a 1 gal bath (number on the abscissa). Results from chrome wash primer (cw) and zinc phosphate (P) are also given.

1.2   Spray Zirconium Pretreatment

1.2.1   Comparison of Spray and Immersion Product Structure

An experiment was designed to evaluate the effect of application method (spray vs. immersion) on coating morphology and performance. Panels were coated under the conditions given in **Table 7**. Using tD1308he same bath chemistries, panels were coated using spray or immersion application methods. Typical formulation practices of zirconium pretreatments utilize more dilute solutions in spray application due to the increased activity from the impingement of pretreatment solution at the surface. The difference in morphology is apparent from the SEM images given in **Figure 17.** The formulas that do not contain copper produce coatings that have few features in both the immersion (**Figures 17a** and **17c**) and spray (**Figures 17e** and **17g**) processes. Both the 200 ppm zirconium (0 ppm copper) variables (**Figures 17c** and **17g**) have the beginnings of nodular features. In contrast, all variables in which copper was present showed nodular features with the nodules of the spray versions (**Figures 17f** and **17h**) having higher density and being more significantly pronounced than the corresponding immersion variables (**Figures 17b** and **17d**).

Panel	H_2ZrF_6	Cu additive	application
a	75	0	immersion
b	75	10	immersion
c	200	0	immersion
d	200	20	immersion
e	75	0	spray
f	75	10	spray
g	200	0	spray
h	200	20	spray
i	zinc phosphate control		

Table 7. Spray and immersion formulations.
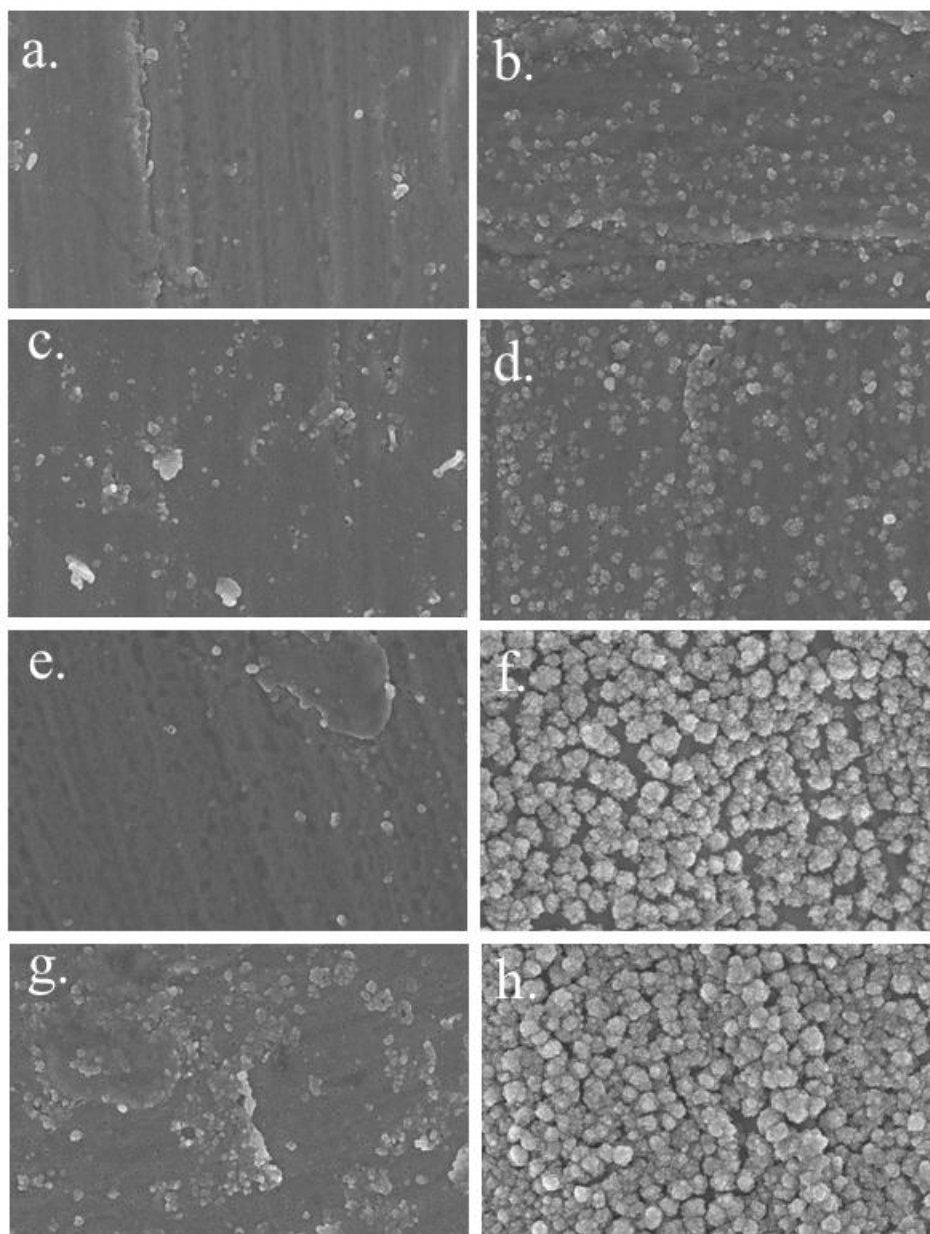
Figure 17. SEM images at 10,000x of (a) H_2ZrF_6, 75 ppm by Zr and 0 ppm of Cu additive applied by immersion. (b) H_2ZrF_6, 75 ppm by Zr and 10 ppm of Cu additive applied by immersion. (c) H_2ZrF_6, 200 ppm by Zr and 0 ppm of Cu additive applied by immersion. (d) H_2ZrF_6, 200 ppm by Zr and 20 ppm of Cu additive applied by immersion. (e) H_2ZrF_6, 75 ppm by Zr and 0 ppm of Cu additive applied by spray. (f) H_2ZrF_6, 75 ppm by Zr and 10 ppm of Cu additive applied by spray. (g) H_2ZrF_6, 200 ppm by Zr and 0 ppm of Cu additive applied by spray. (h) H_2ZrF_6, 200 ppm by Zr and 20 ppm of Cu additive applied by spray.

The spray and immersion processes with the same formula conditions were also evaluated for adhesion and cyclic corrosion on CRS. In impact and 1/4" mandrel bend testing, the immersion applied pretreatments outperform the spray pretreatments (with subsequent

solvent-borne epoxy primer applied). In these tests, the zinc phosphate control and the commercial immersion formula (applied by immersion) performed well. In GMW14872 testing, the immersion application of the commercial spray formula and the commercial immersion formula outperformed the zinc phosphate controls (3.4 and 4.0 vs. 4.9 mm scribe creep, respectively). The spray-applied zirconium formulas performed similarly to the zinc phosphate controls (~5.0 mm). Results are also given in **Figure 18**.
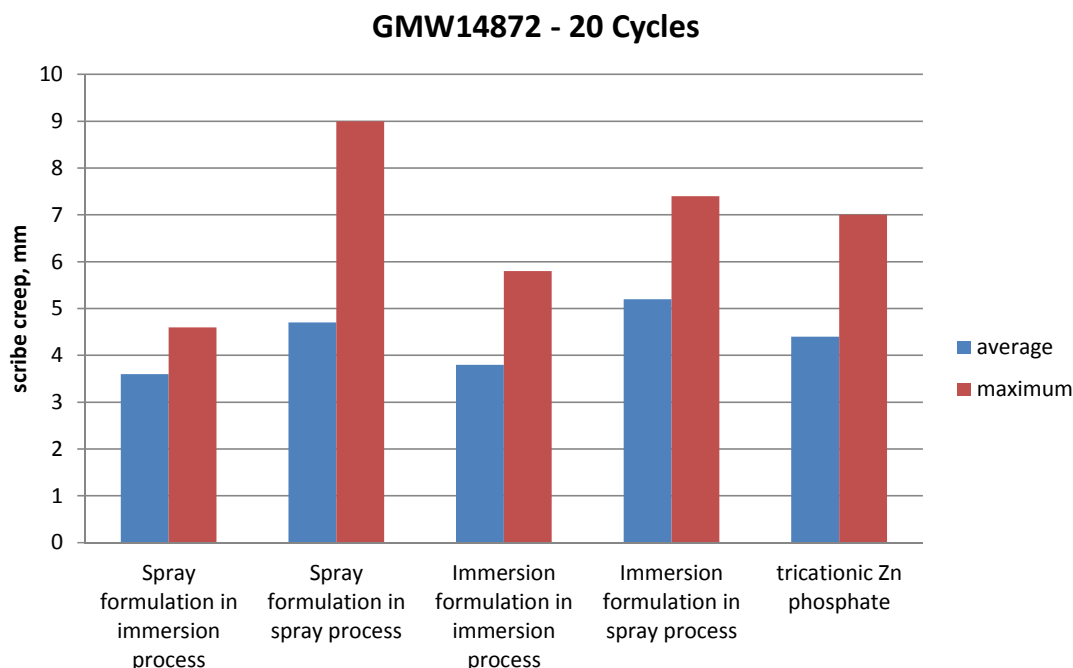
Figure 18. 20 Cycles GMW14872: Spray zirconium formulation vs immersion formulation and zinc phosphate control on CRS

1.2.2 Testing of Spray Pretreatment with DoD Paint Systems

An initial benchmarking set of spray-applied zirconium pretreatments was generated and sent to ARL to be coated with MIL-DTL-53022 and MIL-DTL-53030. The samples included the commercial spray-applied zirconium pretreatment Zircobond4200 with and without copper. The spray applied systems are typically formulated similarly to the immersion formulations, although at a lower concentration as described above. Samples were evaluated by ASTM D3359 (adhesion testing), ASTM D1308 (water-immersion testing), and by JP8 fluid immersion (adhesion testing). Results from the first round of testing on the spray Zircobond4200 formulas did not pass the MIL-DTL-53022 and MIL-DTL-53030 specifications (see **Table 8**). Further formulation work was necessary.

	Test	Standard	Zinc phosphate	Chrome(VI) wash primer	Zircobond4200 spray formulation (10 ppm of Cu)	Zircobond4200 spray formulation no Cu additive
Cold-rolled steel, water-reducible primer (MIL-DTL-53030)	Wet/dry adhesion	ASTM D3359	5B	5B	2B	3B
	Water immersion	ASTM D1308	5B	4B	4B	2B
	JP8 fluid immersion	-	5B	5B	3B	2B
Cold-rolled steel, solvent-borne primer (MIL-DTL-53022)	Wet/dry adhesion	ASTM D3359	5B	4B	2B	1B
	Water immersion	ASTM D1308	4B	4B	3B	0B
	JP8 fluid immersion	-	4B	4B	3B	2B

Table 8. Adhesion of CARC coating system (Ratings of 4B and 5B were considered passing values)

1.2.3 Modification/Optimization of Bath Composition for Spray Application

The spray optimization portion of this project used the lessons learned during the modification of the immersion formula to accelerate the development process. Accordingly, an initial experiment was conducted with Zircobond4200 at 0 and 10 ppm of copper, at 20 and 80 ppm of F$^-$, and with H$_2$SiF$_6$ and H$_2$TiF$_6$ adhesion promoters (20 ppm of metal each). After 20 cycles of GMW14872, the pretreatment at 80 ppm of free fluoride was again found to be an improvement over the Zircobond4200 spray control (see **Figure 19** for GMW14872 data). Additional benefits in GMW14872 were observed with the addition of 10 ppm of copper. The combination of increased F$^-$ and 10 ppm of copper showed the best performance in GMW14872. In 500 hours ASTM B117, however, adding additional F$^-$ showed no improvement in corrosion. But again, the combination of increased F$^-$ and 10 ppm of copper was the best-performing system (see **Figure 20**).

As mentioned previously, ZrO(NO$_3$)$_2$ was successfully deposited in a immersion application with hexafluorozirconic acid or other metal salts. A corrosion study was also conducted to determine if ZrO(NO$_3$)$_2$ - based pretreatments can be applied on CRS using a spray application method and then perform well in testing. In the initial experiments, the ZrO(NO$_3$)$_2$ - based pretreatments performed similar to Zircobond4200, and modestly better in GMW14872 cyclic corrosion testing under epoxy primer. Due to the lack of performance improvement in the DoD required tests, as well as the cost of the inhibitors investigated, no further work was conducted using the alternative zirconium source.
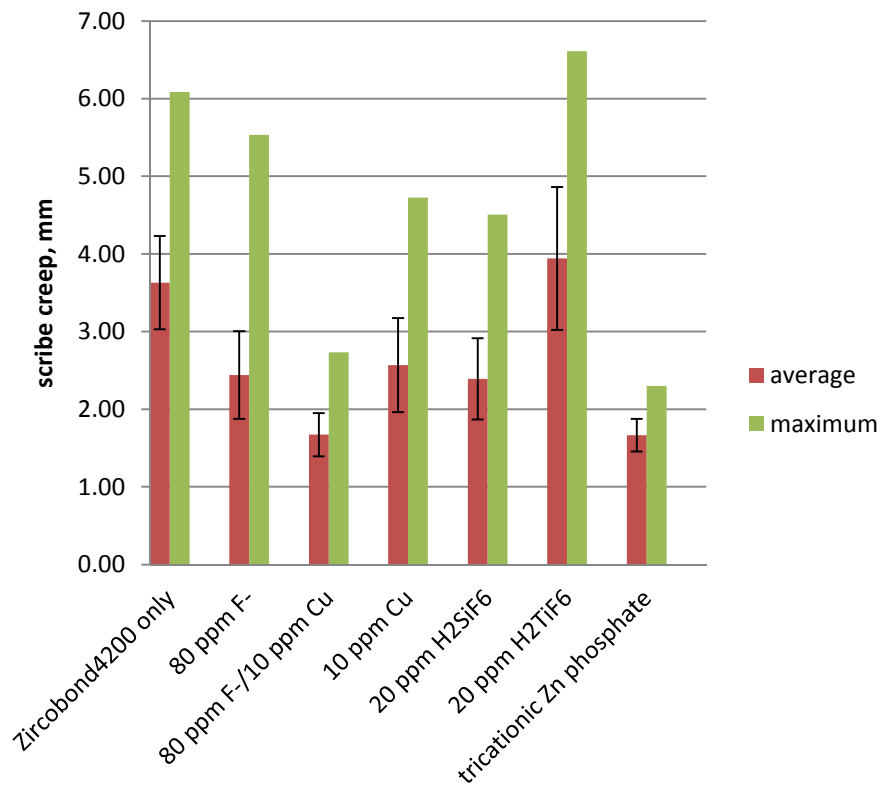
Figure 19. Zircobond4200 spray with the additives outlined above in 20 Cycles GMW14872 on CRS.
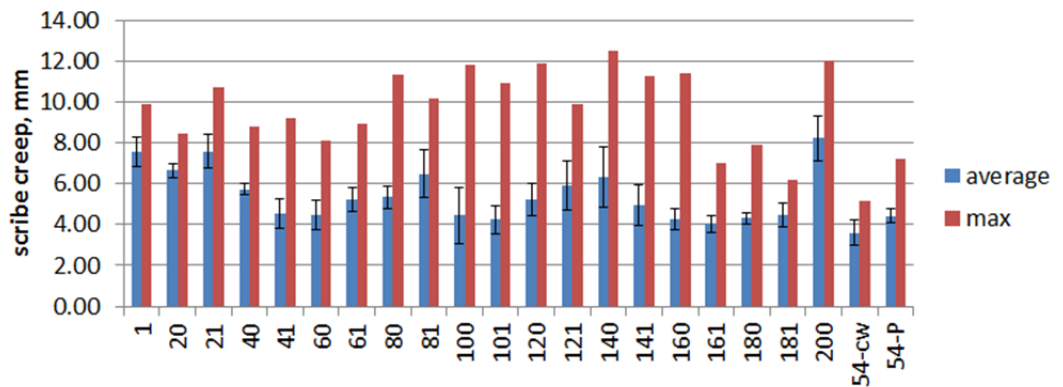
Figure 20. Zircobond4200 spray with the additives outlined above in 500 hours ASTM B117 on CRS.

Based on all the test data, the best performing system was found to be Zircobond4200 modified to increase the free fluoride level by 60 ppm (~80 ppm total). Using these results, it was agreed to conduct limited military specification testing on the spray-applied zirconium pretreatments including the Zircobond4200 spray, as well as with samples containing additional F⁻ and/or copper. Cold-rolled steel panels were pretreated and shipped to ARL for painting with MIL-DTL-53022 or MIL-DTL-53030 epoxy primer. The first round of testing included ASTM D3359 (adhesion test), ASTM D1308 (water-immersion testing), and JP8 fluid immersion (adhesion test).

Zircobond4200 was tested with and without copper as part of the previous task (See **Table 9**). In this test, Zircobond4200 with copper performed slightly worse in corrosion testing than the controls. With the formula modifications, including the addition of 60 ppm F⁻ (~80 ppm total) to Zircobond4200 spray (akin to the modifications made to the immersion formulas), both samples passed the first round of specification testing (see **Table 10**). However, the system with no copper performed poorer than the system with 10 ppm copper. This result is the opposite of what is observed in the immersion formulation. It is not well understood why a small amount of copper is an advantage in the spray application, however, the morphology of spray is unique when compared to immersion application. A more nodular structure is observed in the spray formula at 10 ppm of copper (see **Figure 17**).

	Test	Standard	Zinc phosphate	Chrome(VI) wash primer	Zircobond4200 spray formulation (10 ppm of Cu)	Zircobond4200 spray formulation no Cu additive	Zircobond4200 spray formulation + 80 ppm of F-	Zircobond4200 spray formulation + 80 ppm of F- + 10 ppm Cu additive
Cold-rolled steel, water-reducible primer (MIL-DTL-53030)	Wet/dry adhesion	ASTM D3359	5B	5B	2B	3B	3B	4B
	Water immersion	ASTM D1308	5B	4B	4B	2B	3B	4B
	JP8 fluid immersion	-	5B	5B	3B	2B	3B	4B
Cold-rolled steel, solvent-borne primer (MIL-DTL-53022)	Wet/dry adhesion	ASTM D3359	5B	4B	2B	1B	3B	4B
	Water immersion	ASTM D1308	4B	4B	3B	0B	3B	4B
	JP8 fluid immersion	-	4B	4B	3B	2B	3B	4B

Table 9. Adhesion of CARC coating system (Ratings of 4B and 5B were considered passing values).

	B-117		GMW14872	
	336 hours	1008 hours	20 cycles	40 cycles
tricationic Zn phosphate	Pass	Pass	Pass	Pass
Chrome(IV) wash primer	Pass	Pass	Pass	Pass
Zircobond 4200 spray with 80 ppm F-	marginal	Fail	marginal	Fail
Zircobond 4200 10 ppm of Cu and 80 ppm of FF-	Pass	marginal	Pass	marginal

Table 10. Spray prototype corrosion performance.

The two samples, Zircobond4200 at 80 ppm of F- with and without 10 ppm of copper, performed similar to zinc phosphate and chrome (VI) wash primers in ASTM D3359 (adhesion test), ASTM D1308 (water-immersion testing), and by JP8 fluid immersion (adhesion test). Based on these results, a follow-up set of panels was requested by ARL for a second round Mil-Spec testing. The two passing formulas were tested in a second round of specification testing which included cyclic corrosion testing (GMW 14872) and neutral salt spray (ASTM B117).

ARL evaluated the two prototype spray formulas in a second stage of testing. Zircobond4200 with 80 ppm of F- and 10 ppm of copper passed the 336 hour salt spray (ASTM B117) requirement, but exhibited some blistering in 40 cycles of GMW 14872 corrosion testing with the water reducible primer system (MIL-DTL-53030).

A second set of panels was requested by ARL for additional adhesion and long-term corrosion testing. This series of panels passed both cyclic and salt-fog testing when coated with the solvent-borne primer system (MIL-DTL-53022). However, all panels, including controls, failed under the water-reducible system (MIL-DTL-53030) suggesting a paint related problem. These samples were again recoated and tested. The results of this final spray test agreed well with earlier testing. The best prototype system, Zircobond4200 spray with 10 ppm of copper and 80 ppm of F-, performed well in short-term testing (i.e. comparable to commercial tricationic immersion zinc phosphate with a chrome-free rinse), but the accelerated long-term performance was not equal to controls for the spray system as noted in **Table 10**. Samples are currently in outdoor exposure testing at NASA's Cape Canaveral beachside corrosion site along with the best immersion pretreatment formulas. This testing will be monitored as part of the WP-201318 ESTCP program.

1.2.4   Spray Turnover Study

A turnover study was conducted with the spray prototype formulation. Four hundred 4x12" panels were run using 2 gallons of prototype spray formula while controlling pH and free fluoride (Zircobond4200 replenisher, ZB4200DR, was used to reduce pH). All work was conducted at pH 4.7, 80°C. This study represents ~2 weeks on a spray production line running a moderate schedule equivalent to two daily shifts for five days a week.

Similar to the immersion study, it was noted that replenishment based on ZB4200DR over this range was not sufficient to maintain zirconium content in the bath (See **Figure 21**). It must be noted that the zirconium content was too low to maintain the Zircobond4200 coating throughout the process for this application. Samples were taken every 20 (prior to bath adjustment) and 21 (after adjustment with ZB4200DR replenisher) panels, coated with the solvent-borne primer system (MIL-DTL-53022) and tested in 20 cycles of GMW14872. Results are given in **Figure 22**. During the initiation of the spray throughput experiment, the scribe creep average was similar to ZB4200 and zinc phosphate controls. At ~200 panels, the insufficient replenishment of zirconium, while replenishing other components, leads to poorer performance. After the 280th panel, replenishment led to a positive change in corrosion performance. While the absolute cause of this improvement is not well understood, it is likely that the increasing levels of ZB4200DR components without the increase in zirconium lead to the formation of a non-zirconium metal oxide such as an iron phosphate or similar coating. To better test the throughput operation of this system, the replenishment study would need to be repeated at the appropriate zirconium level.
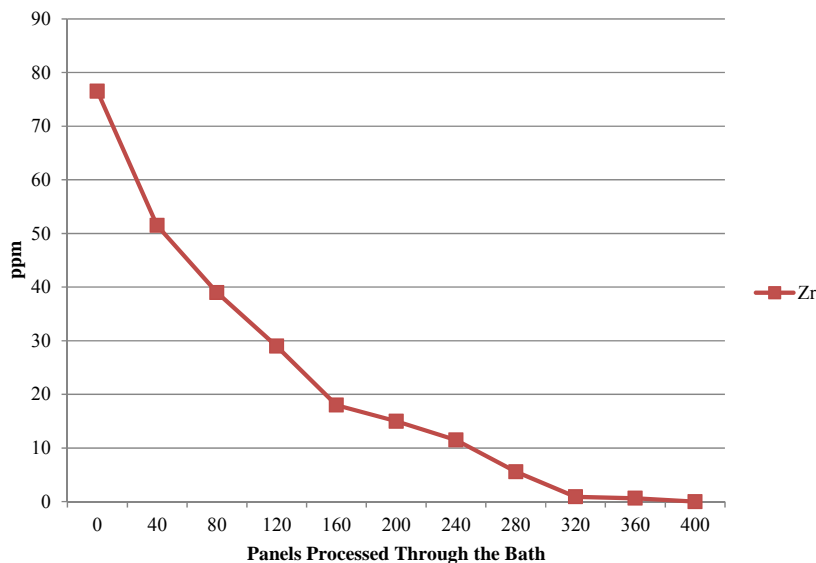
Figure 21. Zircobond4200 spray prototype Zr content by using an ICP to measure Zr.
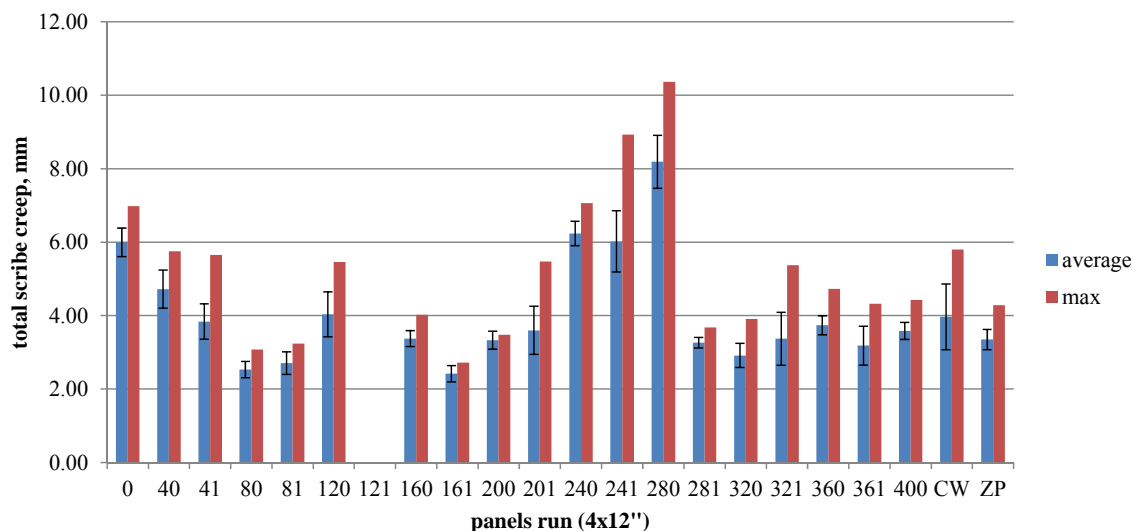
Figure 22. Zircobond4200 spray prototype tested in 20 cycles of GMW14872 after a given number of panels were run through a 2 gal spray bath (number on the abscissa). Results from chrome wash primer (cw) and zinc phosphate (ZP) are also given.

Both the spray and immersion throughput studies highlight the need for further replenishment development for these prototype systems to become fully commercial. Additionally, the studies show that the immersion system is quite robust even at greatly reduced zirconium content. For the spray system, the replenishment system was not successful in retaining the zirconium content over the duration of the study. It must be noted that even at very low levels of zirconium performance in GMW14872 is retained. While it is surprising that the corrosion performance is retained, it is recognized that the result would need to be repeated with an appropriate replenisher to determine relevance to field operation.

2 Development of Spray Applied Pretreatment for Depot Application

The goals of this task were to first understand the needs of DoD depots by visiting them and discussing their requirements, and then to use this information to create a pretreatment to fit into their infrastructure as a chrome wash primer replacement. After evaluating the needs of the depots, the formulations created as part of Task 1 were used as model formulations for the development of new pretreatments suitable for the DoD repair environment.

2.1 Depot Operation Survey and Pretreatment Compatibility / Modification Assessment

Work was conducted as part of this task to promote the project and zirconium pretreatment technologies to the DoD community. ARL was instrumental in finding opportunities at depots to promote zirconium-based chemistry, in ensuring success in future

activities by attending DoD-sponsored meetings, and in presenting data developed under this project.

Work associated with this project was presented at the following conferences to promote the progress of the project:

- US ARMY Corrosion Summit, February 9-11, 2010 (seminar)
- 1109th Aviation Classification Repair Activity Depot Workshop, June 23, 2010 (seminar)
- TARDEC Paint Forum, February 1, 2011 (seminar)
- DoD Corrosion Conference, July 31 to August 5, 2011 (seminar/paper)
- ASETSDefense Conference, August 27-30, 2012

An important goal of Task 2 was to survey representative depots to determine their capabilities and needs. ARL personnel organized an on-site visit to the Marine depot facilities Marine Corps Logistics Base Albany, in Albany, Ga., which was held 1/13/10. Vital information was obtained regarding depot processes and capabilities pertaining to metal cleaning, pretreatment, and painting.

A tour was also conducted at the Letterkenny Army Depot, Chambersburg, Pa., on 5/18/10. The visit was useful to help understand the application methods that would be necessary to be compatible with current depot setups and to develop a network of depot personnel interested in the new technologies that were developed under this contract. ARL has stayed in constant contact with Letterkenny personnel to update progress. Letterkenny personnel are willing to be a possible test site for a final product once testing is complete.

The two depot visits highlighted several opportunities for use of not only a Dried-In-Place zirconium pretreatment to directly replace chrome-based wash primers, but also a need for immersion based pretreatments for aluminum (Letterkenny) and CRS (Letterkenny and Albany). Zirconium pretreatments have the potential to help minimize the environmental impact of these facilities by replacing chrome (VI) wash primers, chrome (VI) conversion coatings for aluminum, and zinc (or other metal) phosphates. A full summary of capabilities and needs for the three sites is given in **Table 11**.

	Letterkenny Army Depot	Marine Corps Logistics Base at Albany, GA	AVCRAD Groton, CT
Substrate	Al and steel	Steel	Al
Wash primer replacement priority	Very high	Medium	Low
Trichrome pretreatment	No	Yes	Yes
Chrome(VI) pretreatment	Yes	Yes	Yes
Zinc phosphate	Yes	Yes	No
Rinsed pretreatment desirable	Minimal rinse	Minimal rinse	Yes
Dry in place pretreatment desirable	Yes	Yes	Yes

Table 11. Depot pretreatment capabilities and needs

2.2 Optimization of Zirconium Pretreatment for Depot Use

The goal of this task was to adapt the pretreatments developed in Task 1 to make them compatible with the application practices and needs identified during the depot site evaluations. It was apparent from these visits that the immersion prototype developed under Task 1 would have direct applicability (in the depot setting at the two sites visited) for application on aluminum and steel substrates (including HHA steel). However, there was also an obvious need to proceed with development of spray-type application that would limit the amount of material that would run off of a work piece and have to be disposed of as waste or reclaimed (see **Table 12** for list of application types at visited depot sites). The current formulations, including the prototype formulations for spray and immersion, are based on a dilute solution of hexafluorozirconic acid. These solutions are <1% solids, with the remaining solution being water. In an OEM spray application the work piece is in continuous contact with the solution by constant spraying via risers for up to 2 minutes (see **Figure 23**). As mentioned above, this type of application does not fit into a depot application due to the requirement of high volume run-off collections. Additionally, this type of process would be cost prohibitive due to required facility modifications that would be required for this type of application. This obstacle may be overcome by modifying the prototype zirconium pretreatment solutions, which have a rheology similar to that of water, so that they will remain on a work piece after application. This approach would allow for extended exposure time of the work piece to the pretreatment without an excessive run-off. While a fully Dried-In-Place system will be discussed further in Task 3, this

intermediate task focused on modifying the rheology of the prototype systems (and their chemistry) to function in Depot applications. Subsequent work has suggested that a fully Dried-In-Place formula is feasible. This system will be further discussed in Task 3.

Rheology modifier	Laponite amount (weight %)	Zr ppm (from hexafluoro zirconic acid)	Cu (ppm)	F- ppm	Panel code
Laponite XL21	3.5	500	20	as-is	1
				+ 80 ppm	2
		1000	40	as-is	3
				+ 80 ppm	4
		5000	200	as-is	5
	3.0	500	20	as-is	6
				+ 80 ppm	7
		1000	40	as-is	8
				+ 80 ppm	9
		5000	200	as-is	10
Laponite OG	3.25	500	20	as-is	11
				+ 80 ppm	12
		1000	40	as-is	13
				+ 80 ppm	14
		5000	200	as-is	15
	2.75	500	20	as-is	16
				+ 50 ppm	17
		1000	40	as-is	18
				+ 50 ppm	19
		5000	200	as-is	20
Standard imm. Zircobond		200	20	+ 80 ppm	21
Clean only (no pretreatment)	alkaline clean only				22
tricationic zinc phosphate					23
Wash Primer					24

Table 12. Formulas with rheology modifications

Figure 23. Typical spray application of zirconium pretreatments using risers.

The prototype zirconium pretreatment material developed in Task 1 was used as the starting point for development. The initial target was to modify the solution rheology to enable it to remain on vertical surfaces. A wide variety of rheology modifiers was considered. These ranged from organic compounds that have van der Waals (or London dispersion) type interactions between molecules to platy-type clay materials which have similar interactions, but typically consist of larger primary particles. However, the rheology modifier selected for this application was required to meet two requirements. 1) The thickener must not prevent deposition of the zirconium oxide coating or negatively affect corrosion performance and 2) the thickener must display non-Newtonian rheology-modifying behavior. While the first point ensures that the coating is deposited, the second point is important for application with spray equipment. Non-Newtonian rheology modifiers have the ability to impart shear-thinning characteristics under high shear conditions, while remaining viscous when the shearing force is removed.[20]

The rheology modifiers that were evaluated were commercially-available synthetic clays which have a much smaller particle size than naturally occurring clays such as Bentonite,[21] and have been found in previous evaluations by PPG to perform well under acidic conditions. These clays resulted in formulas displaying non-Newtonian rheology which resulted in good sprayability under high-shear conditions, as well as causing the sprayed coating to immediately thicken upon application to the vertical work piece surface. The resulting increased contact time on the surface also aids in preventing the formation of flash rusting resulting from the interaction of CRS with an acid containing material and subsequent exposure to oxygen. When a water-thin commercial zirconium pretreatment is applied on a vertical surface for 10 minutes, flash rusting is formed and intermixes with the deposited zirconium. The addition of ~2% of a non-Newtonian rheology modifier to a water-thin commercial zirconium pretreatment was found to be effective for mitigating flash rusting (see **Figure 24**). Note that, because of the limited run-off of the pretreatment, these systems then required a rinse after application time is completed. A subsequent drying step completed the process.
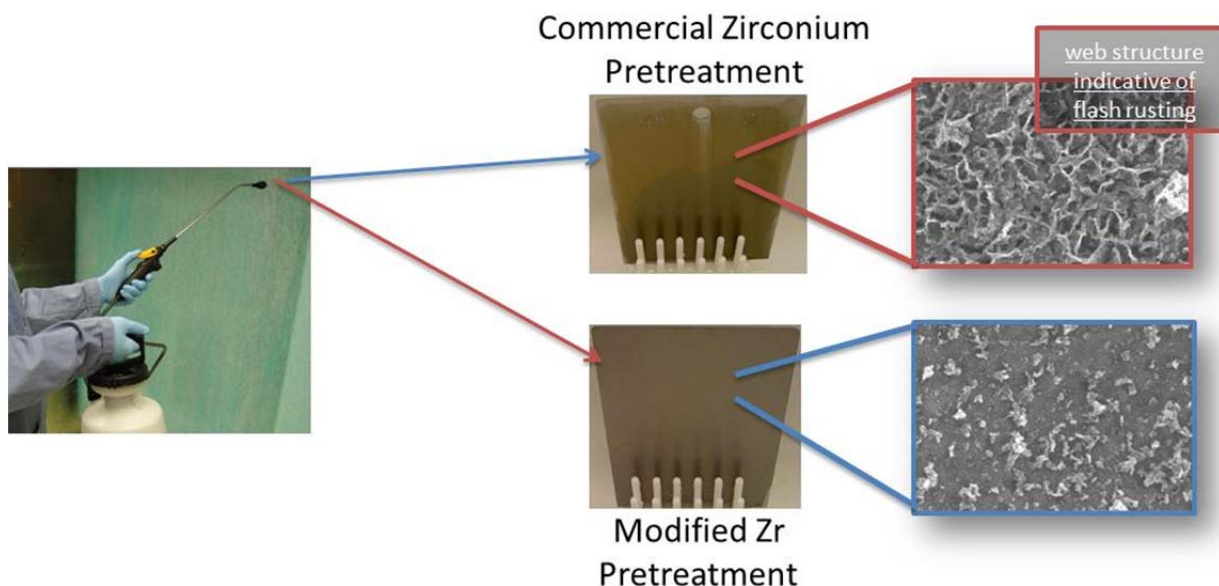
Figure 24. Panels (and SEM images at 5000x) coated vertically with the commercial zirconium pretreatment system and the same system modified with a non-Newtonian rheology modifier.

Zirconium pretreatments were modified in the following manner. The Laponite was slowly added to water while agitating vigorously using a Cowles dispersion blade until a 3% (w/w) dispersion was achieved. When the solution thickened substantially, the pH was adjusted from pH ~10 to a pH <5 using dilute nitric acid to ensure that the stability of the solution upon the subsequent addition of the hexafluorozirconic acid, which becomes insoluble at about pH 6.

Zirconium pretreatments that were initially modified with Laponite XL21 and OG were successfully applied to vertically-oriented panels with no apparent flash rusting after 5 and 10 minutes contact time (single application). An integral coating, with a unique morphology, was formed on cold-rolled steel as observed by EDS and SEM. The SEM image in **Figure 25** compares the morphology of the commercial zirconium pretreatment and the system modified with Laponite XL21. The system modified with Laponite XL21 has larger structural features than the commercial system. The system modified with Laponite XL21 was also evaluated by EDS to determine if zirconium was deposited. The EDS spectrum (given in **Figure 26**) shows a distinct peak indicating deposition of zirconium.
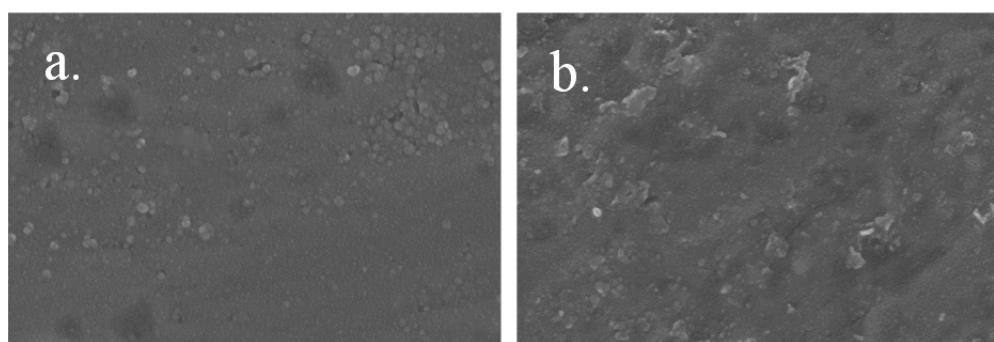
Figure 25. SEM images at 60,000x of (a) the commercial zirconium pretreatment and (b) the commercial zirconium pretreatment which has been thickened.
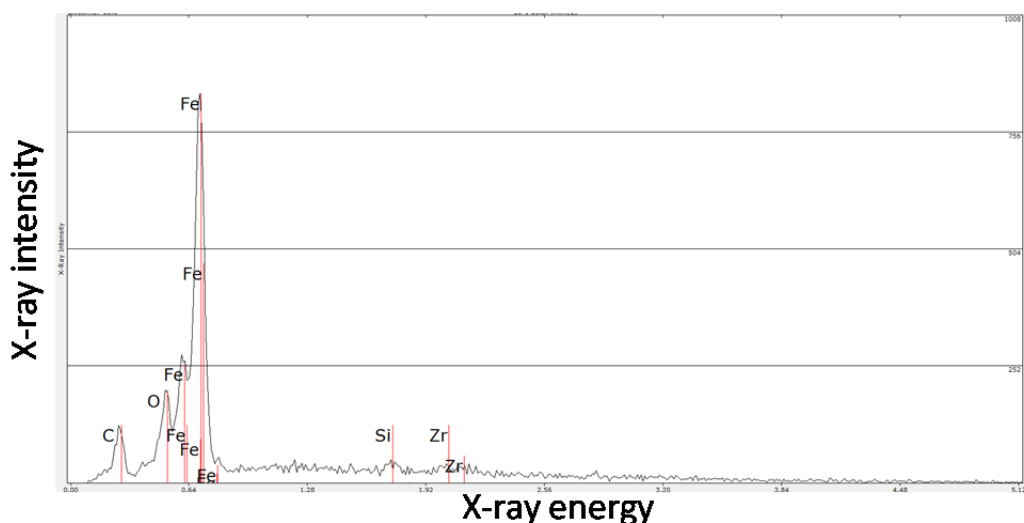
Figure 26. EDX spectrum of the rheology modified zirconium pretreatment applied to a vertical surface.

Panels were treated with the Spray-On/Rinse-Off zirconium systems modified with Laponite XL21 and OG, then subsequently coated with the solvent-borne primer system (MIL-DTL-53022). The panels were evaluated for corrosion resistance using GMW14872 cyclic testing (20 cycles), and ASTM B117 salt spray (500 hours). In all cyclic tests, the rheology-modified formula performed comparably to the immersion applied prototype zirconium formula as well as to the zinc phosphate control (see **Figure 27**). The rheology-modified system performed modestly worse in ASTM B117 neutral salt spray testing, and for some samples, substantially worse (see **Figure 28**). In cyclic testing, the zirconium system with Laponite OG at low zirconium levels, and high Laponite levels performed poorly. In this system it is likely that the hexafluorozirconic acid could not provide adequate zirconium deposition in the presence of the clay resulting in total delamination in the test. In salt spray, a number of the systems modified with the OG performed poorly, along with some of the Laponite XL21-modified samples at the highest zirconium level. The poor performance resulted in total delamination for a number of samples (See **Figure 28**). This experiment suggested that an intermediate level of zirconium (lower than 5000 ppm) and Laponite XL21 should result in improved performance. In addition to the corrosion testing, it was noted that the long-term (1 month or greater) storage stability of the Laponite OG system was poor, while the stability of the Laponite XL21 was quite good.

Next, an experiment was conducted to determine the optimum level of hexafluorozirconic acid (as ppm of zirconium) and the necessity of copper in the Spray-On/Rinse-Off prototype. Samples were coated with pretreatments containing 3% Laponite XL21, 1000 or 2000 ppm of zirconium, and 0-100 ppm of copper. The samples were then coated with the solvent-borne primer system (MIL-DTL-53022) and placed in 500 hours salt spray. After 500 hours of salt spray, it was apparent (see **Figure 29**) that >10 ppm copper was not beneficial to performance. Additionally, the 1000 ppm zirconium (from hexafluorozironic acid) outperformed the 2000 ppm zirconium formula.
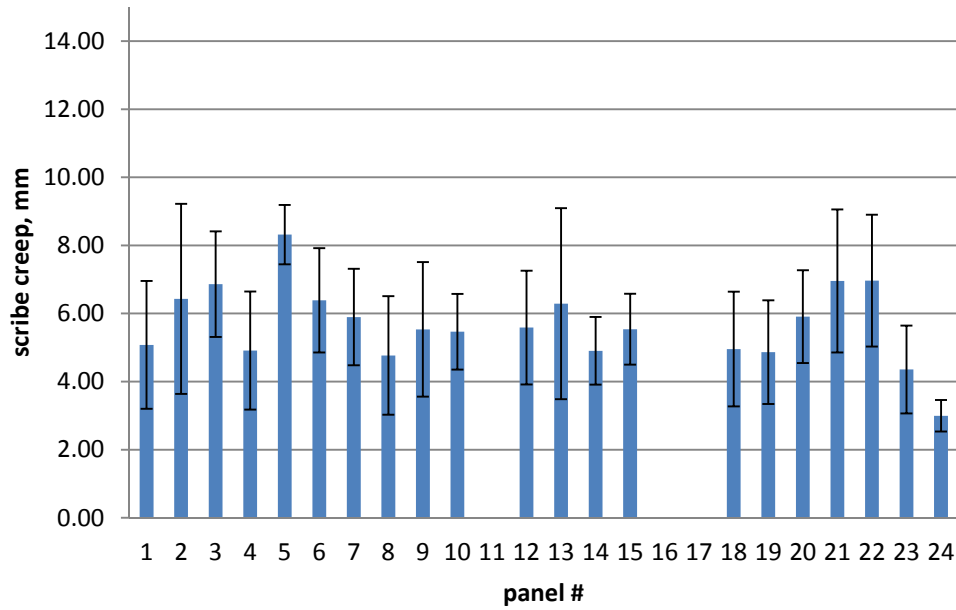
Figure 27. Samples evaluated by 20 cycles GMW14872. Key given in Table 13. Missing bars represent total delamination.
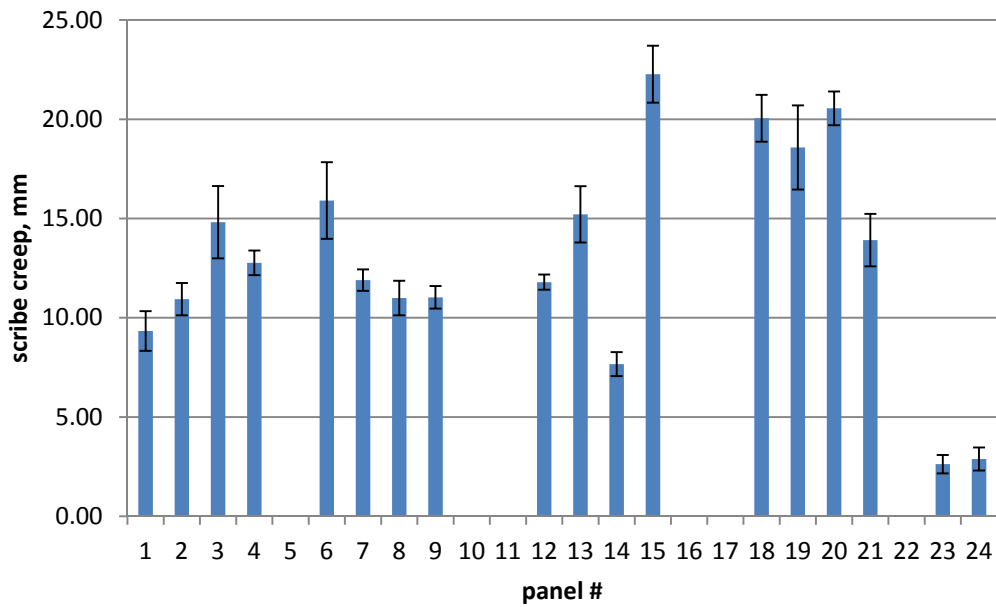
Figure 28. Samples evaluated by 500 hours ASTM B117. Panels are described in Table 13. Missing bars represent total delamination.
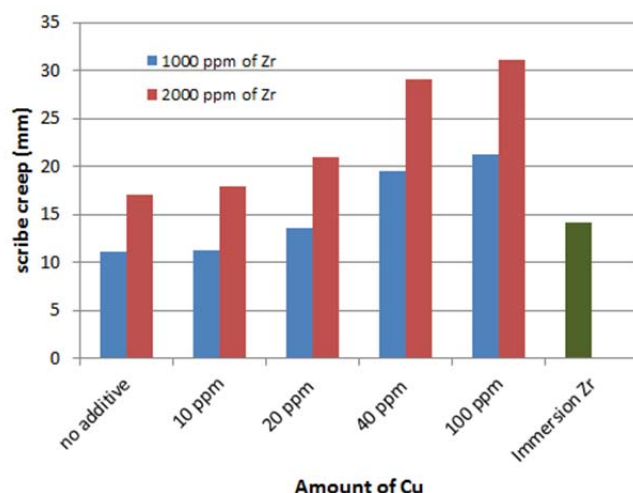
Figure 29. Effect of Zr concentration and level of Cu on CRS after 500 hours ASTM B117.

The best-performing rheology-modified system consisted of 3% Laponite XL21, 1000 ppm zirconium (from hexafluorozirconic acid), and 10 ppm of copper. The prototype performed equal to the Zircobond4200 (without copper) in GMW14872 and only modestly lower than the immersion formula in ASTM B117. The Laponite XL21 was optimal in imparting the required non-Newtonian rheology, as well as in retaining the rheological characteristics upon extended storage. Samples of the prototype system were then sent to ARL for Mil-Spec testing.

2.3   Performance Testing with CARC Paint Systems

Panels were prepared using the prototype Spray-On/Rinse-Off system from Task 2.3 and submitted to ARL for painting and evaluation. Panels were received by ARL and coated with MIL-DTL-53022 (for solvent-borne) and MIL-DTL-53030 (water- reducible) primers. Panels were evaluated for adhesion performance using guidelines detailed in MIL-DTL-53022 and MIL-DTL-53030.

After exposure to water immersion or JP8 fluid, no change in color gloss or hardness was observed. Initial adhesion of the water reducible system was a 3B. Water immersion had a slight detrimental effect on adhesion for both paint systems. Additionally, JP8 fluid immersion had a slightly detrimental effect on adhesion. Results from ASTM D3359, ASTM D1308, and JP8 fluid testing for the solvent and water reducible systems are given in **Table 13**.

	Test	Standard	Zinc phosphate	Chrome(VI) wash primer	Spray on/rinse of prototype
Cold-rolled steel, water-reducible primer (MIL-DTL-53030)	Wet/dry adhesion	ASTM D3359	5B	5B	3B
	Water immersion	ASTM D1308	5B	4B	3B
	JP8 fluid immersion	-	5B	5B	3B
Cold-rolled steel, solvent-borne primer (MIL-DTL-53022)	Wet/dry adhesion	ASTM D3359	5B	4B	4B
	Water immersion	ASTM D1308	4B	4B	3B
	JP8 fluid immersion	-	4B	4B	3B

Table 13. Results from ASTM D3359, ASTM D1308, and JP8 fluid testing for the solvent and water reducible systems.

A process demonstration of the Spray-On/Rinse-Off prototype system was conducted at ARL, Aberdeen Proving Ground, in March 2012. The ARL personnel observed the successful application of the prototype to cold-rolled steel panels, and brought issues to light including the shelf stability. Additionally, an extended dry-off condition was tested at ARL, which resulted in a gold color on the surface of the panels, which suggested the possibility of flash rusting.

Based on this feedback, PPG tested a number of factors to determine their impact on long-term storage stability. It was determined that process time and mixing speed had a significant impact on stability, as measured by visual inspection and viscosity, as well as batch-to-batch reproducibility. With this information, a three gallon sample of the Spray-On/Rinse-Off material was prepared and has maintained stability for 16 months.

Experiments were conducted in an attempt to mitigate the golden color that was suggestive of flash rusting that appeared after the application of the pretreatment during the ARL application. Two approaches were taken to address this issue. The first was to develop a rinse solution that would inhibit the formation of flash rust. The second was the addition of rust inhibitors directly into the treatment.

First, sodium nitrite (100 ppm) was dissolved in deionized water and used as a post rinse. Second, sodium hydroxide (0.12%) was added to the deionized water to achieve solution pH of 10. These solutions were used to rinse CRS panels treated with the Spray-On/Rinse-Off prototype. Sodium nitrite was also evaluated as an inhibitor in the Spray-On/Rinse-Off pretreatment by adding 100 ppm to the prototype solution. It was also postulated that a higher amount of flash rust occurs when high amounts of the treatment are applied, especially along the edges, so a variable was included to apply a lighter mist of zirconium. Results suggest that none of the rinse or composition changes mentioned above were sufficient to reduce the flash rust (see **Table 14**).

Pretreatment	Rinse	Flash Rust Appearance	Other observations
Spray-On/ Rinse-Off	Deionized Water	Flash rust	Heavy along the edges
Spray-On/ Rinse-Off	100 ppm sodium nitrite	Moderate flash rust	Heavy along the edges
Spray-On/ Rinse-Off	100 ppm sodium nitrite	Moderate flash rust	Heavy along the edges
Spray-On/ Rinse-Off	pH=10 w/ sodium hydroxide	Moderate flash rust	Heavy along edges
100 ppm sodium nitrite misted	Deionized Water	Flash rust	Worse than the control
100 ppm sodium nitrite misted	Deionized Water	Flash rust	Worse than control

Table 14. Flash Rust appearance of Spray-On/Rinse-Off zirconium pretreatment with sodium nitrite and sodium hydroxide with post rinses on CRS.

A second experiment was carried out in which sodium nitrite was added at a higher level (5000 ppm) in the treatment and/or the post-processing rinse. Additionally 2-Amino-2-methyl-1-propanol (AMP95) was evaluated as part of the treatment and/or post rinse. Neither post rinsing with sodium nitrite or the AMP95 modification resulted in any improvement. However, a higher level of sodium nitrite in the pretreatment (5000 ppm) significantly reduced the flash rusting (see **Table 15**). Samples treated with the prototype solution with 0 and 5000 ppm of sodium nitrite were also tested to determine if the addition of the flash rust inhibitor was detrimental to the deposition of the zirconium. Samples were measured using XRF. A sample containing 5000 ppm of sodium nitrite was found to be slightly thinner (44 nm) than the control (53 nm) without inhibitor (see **Table 16**).

Treatment	Rinse	Red Rust
NO INHIBITOR	Deionized water	Flash rusting during final drying
5000 ppm $NaNO_2$	Deionized water	No Flash Rust
SORO w/0.35% AMP-95	Deionized water	Flash rusting during final drying
NO INHIBITOR	0.5% NaNO2	Flash rusting during final drying
NO INHIBITOR	0.35% AMP-95	Flash rusting during final drying

Table 15. Flash Rust appearance of Spray-On/Rinse-Off zirconium pretreatment with sodium nitrite and AMP95 in the treatment and in rinses on CRS.

Treatment	Rinse	Zirconium thickness
NO INHIBITOR	Deionized water	53 nm
5000 ppm $NaNO_2$	Deionized water	44 nm

Table 16. XRF zirconium thickness measurements of Spray-On/Rinse-Off treatment with 5000 ppm sodium nitrite.

As a result of this work, additional experiments were carried out to optimize the level of sodium nitrite in the Spray-On/Rinse-Off zirconium pretreatment. Solutions were made in which the sodium nitrite concentration was varied from 2000-3000 ppm. The results suggest that the sodium nitrite level must be at least 2200 ppm to significantly reduce flash rusting (see **Figure 30**). These samples were also coated with MIL-DTL-53022 (for solvent-borne) and tested in 20 cycles GM14872. The corrosion data shows that the scribe corrosion of all of the samples was slightly worse than the control without sodium nitrite. All of the samples were worse than the zinc phosphate control (photos given in **Figure 31**).
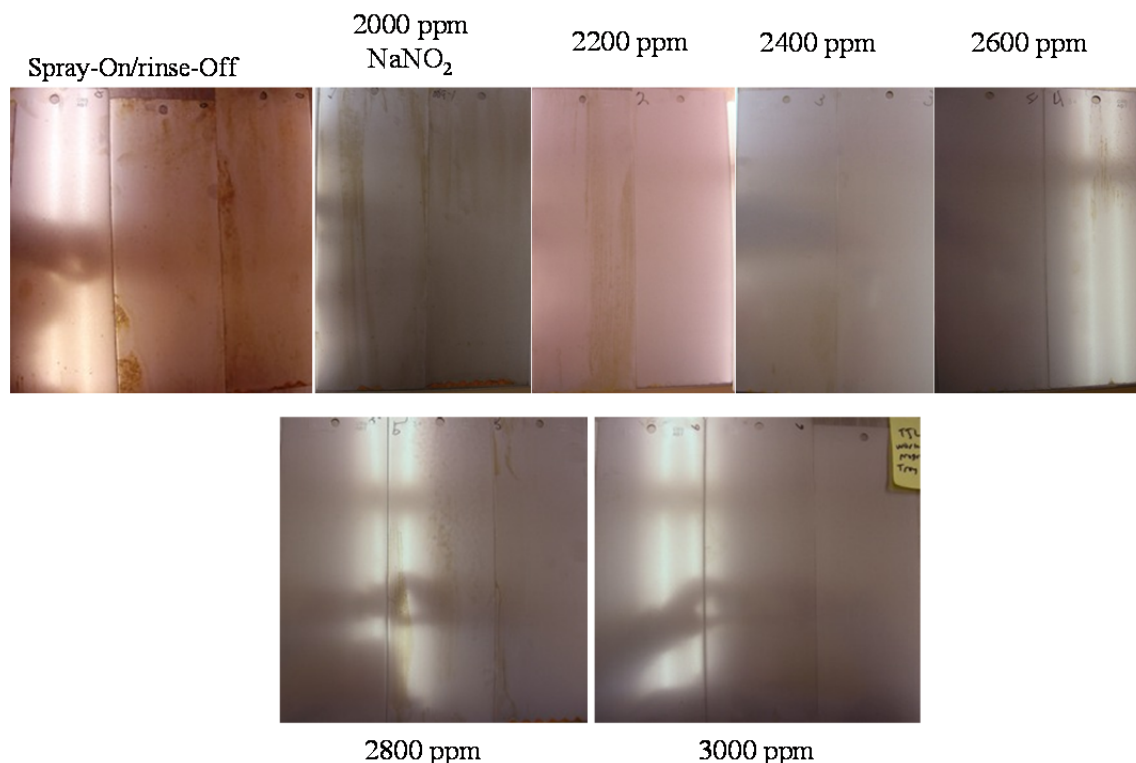
Figure 30. Flash rust appearance of Spray-On/Rinse-Off zirconium treatment with varying levels of sodium nitrite added.

Additional flash rust inhibitors were evaluated in the Spray-On/Rinse-Off zirconium treatment as part of this task. These included Drewgard 795 SA (Sodium Nitrite), ammonium benzoate, sodium molybdate, Flash-x 330 (N,N-Dimethylethanolamine), Raybo 60 No Rust (sodium nitrite, alkylamine), Hold Tight 102 (amine) Nubirox FR-20 (Dimethylethanolamine). No improvement in flash rusting was seen when these materials were used at the suppliers' recommended levels.

The experiments above demonstrated that sodium nitrite can be successfully used to prevent flash rusting of the Spray-On/Rinse-Off version of the zirconium pretreatment on cold rolled steel. Several commercially available anti-flash rust additives were also tested, in the Spray-On/Rinse-Off zirconium pretreatment formula, however, only sodium nitrite was successful. Corrosion testing of the Spray-On/Rinse-Off formula with sodium nitrite shows the sodium nitrite to weaken the corrosion resistance of the Spray-On/Rinse-Off product.
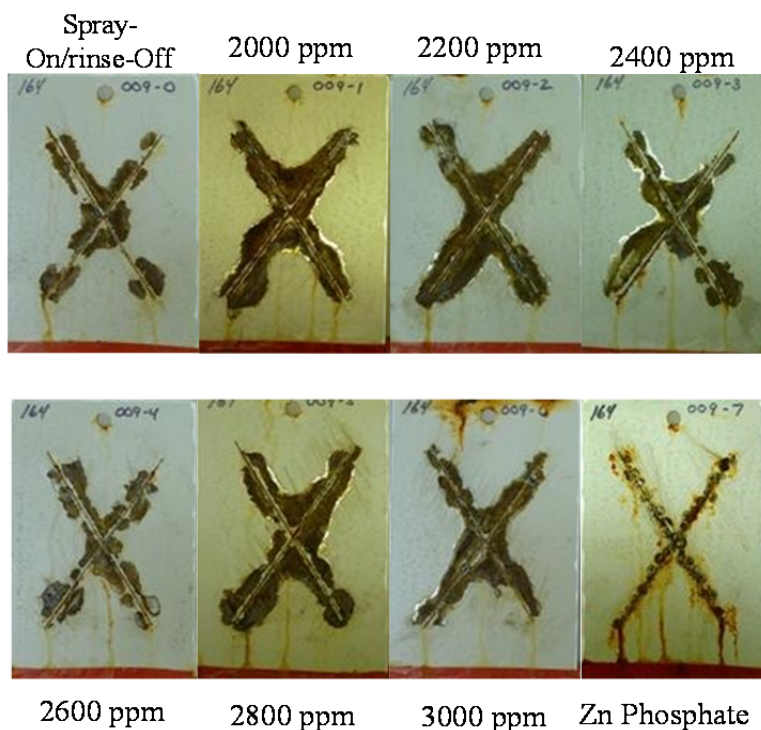
Figure 31. GMW14872 (40 cycles) cyclic corrosion resistance of Spray-On/Rinse-Off zirconium treatment with varying levels of sodium nitrite added.

3 Spray Applied Pretreatment Development for Repair

3.1 Benchmark Testing of Current Baseline

Additional work on a field-applied zirconium pretreatment was directed toward developing a spray-applied pretreatment process in which the pretreatment is sprayed onto the substrate, and then allowed to dry prior to being primed and top coated. This process would eliminate the need to handle waste material from a rinsing step or run-off from the application. It would also reduce the amount of water used in the Spray-On/Rinse-Off process.

Initial benchmarking was conducted by using the best prototype formulas from the immersion task (Zircobond4200 without copper), although at a 10:1 water dilution. The more dilute conditions are required to raise the pH to ~6 and to reduce the level of flash rusting with the dried-in-place application. The Dried-In-Place formulation was evaluated along with the prototype Spray-On/Rinse-Off formula and benchmarked against zinc phosphate immersion pretreatment (CRS), MLB875 Chrome Wash Primer from NCP, and Alodine 1200S (aluminum). The benchmark was carried out on CRS and aluminum, under MLN1981T, a MIL-DTL-53022B Type II solvent-borne epoxy primer from NCP. Samples were also evaluated in ASTM B117 Salt Spray (1000 hours) and in 40 cycles GMW14872). Salt spray was carried out past the 336 hour TT-C-490 specification to differentiate performance. Results show the Dried-In-Place pretreatment outperforms the Spray-On/Rinse-Off prototype, but performs slightly worse than zinc phosphate and chrome wash primer. Results are given in **Tables 17** and **18**. Images are

given in **Figure 32**. Results from this study suggested that the formula would need to be improved to perform equal to the control systems. This work is outlined below.

Substrate	Treatment	Primer	Dry Adhesion	Average Scribe Creep	Average Maximum Scribe Creep
Cold Rolled Steel	Chemfos 700 zinc phosphate	MLN1981T	5B	6.7mm	11.4mm
Cold Rolled Steel	MLB875 Chrome wash primer	MLN1981T	5B	1.5mm	3.0mm
Cold Rolled Steel	Spray-On/Rinse Off Zirconium	MLN1981T	5B	0.4mm	9.3mm
Cold Rolled Steel	Dried-In-Place Zirconium	MLN1981T	5B	1.7mm	8.9mm

Table 17. Benchmark Corrosion Resistance of the Initial Dried-In-Place Treatment versus Zinc Phosphate and Chrome Wash Primer in 1000 hours ASTM B117 Salt Spray Corrosion Testing

Substrate	Treatment	Primer	Dry Adhesion	Average Scribe Creep	Average Maximum Scribe Creep
Cold Rolled Steel	Chemfos 700 zinc phosphate	MLN1981T	5B	1.8mm	5.2mm
Cold Rolled Steel	MLB875 Chrome wash primer	MLN1981T	5B	1.1mm	5.1mm
Cold Rolled Steel	Spray-On/Rinse Off Zirconium	MLN1981T	5B	2.2mm	8.3mm
Cold Rolled Steel	Dried-In-Place Zirconium	MLN1981T	5B	1.7mm	6.4mm

Table 18. Benchmark Corrosion Resistance of the Initial Dried-In-Place Treatment versus Zinc Phosphate and Chrome Wash Primer in 40 cycles GMW14872 Cyclic Corrosion Testing.
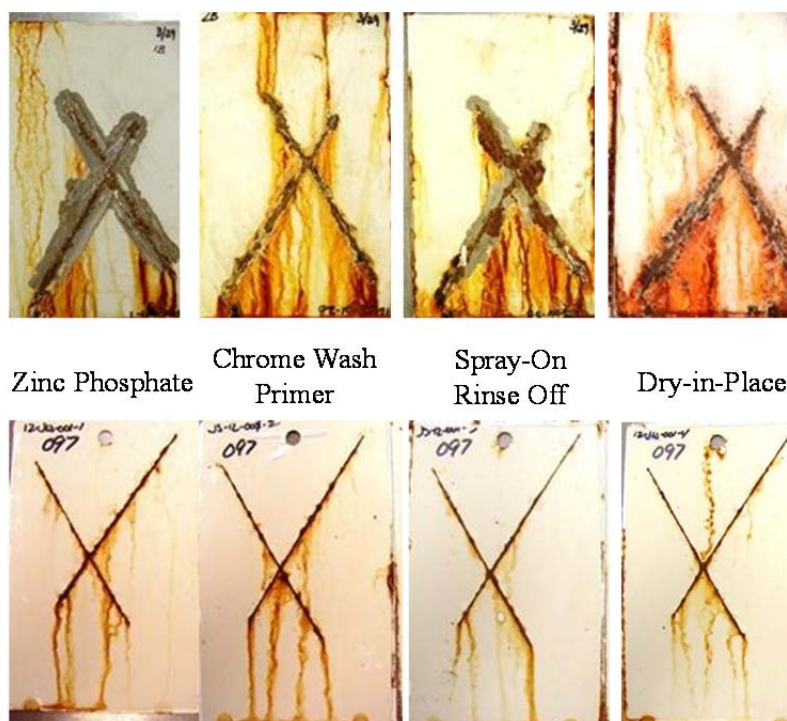
Figure 32. (top) Benchmark ASTM B117 Salt Spray Corrosion Testing (1000 hours) of the zirconium Spray-On/Rinse-Off and Dried-In-Place field-applied Treatments on CRS under MLN1981T MIL-DTL-53022B solvent-borne epoxy primer. (bottom) Benchmark GMW14872 Cyclic corrosion Testing (40 cycles) of the zirconium Spray-On/Rinse-Off and Dried-In-Place field-applied Treatments on CRS under MLN1981T MIL-DTL-53022B solvent-borne epoxy primer.

3.2   Reformulation and Testing of Zirconium Pretreatment

Results from the benchmarking study suggested that improvements in corrosion performance would be necessary for the Dried-In-Place formula to equal that of zinc phosphate. The first approach to improving the corrosion of the DIP formula was the addition of adhesion promoters and cathodic/anodic corrosion inhibitors.

Based on previous work with the zirconium treatment, modified DIP treatment samples were prepared by adding small amounts of inorganic metal salts of cerium (cathodic inhibitor)[22] and molybdate (anodic inhibitor)[23] or hydroxy-functional organic acid (as an adhesion promoter)[24] and organic acid-modified metal salt (a cathodic and anodic inhibitor)[25] added at 0.5%. These samples gave better corrosion resistance in GMW14872 than the control DIP formula and performance equal to or better than the zinc phosphate control on CRS. Results of this experiment are shown in **Table 19** and **Figure 33**.

A follow-up experiment was conducted to better evaluate the positive signal seen with the addition of the organic acid-modified metal salt. Work was initiated to optimize the level of the additive in the DIP zirconium treatment. The original experiment tested this organic acid-modified metal salt at 5000 ppm on solution and at 1000 ppm zirconium, so a subsequent series of experiments was conducted at levels of 5000 ppm, 2000 ppm, and 1000 ppm organic acid-

modified metal salt and at 1000, 200 ppm, and 25 ppm zirconium. The data showed that at 5000 ppm of the organic acid-modified metal salt and 200 ppm zirconium, slightly better performance is achieved versus the control DIP zirconium system in GMW14872, and better performance than the control in ASTM B117. All of the zirconium pretreated samples were worse than zinc phosphate in this experiment. **Figure 34** shows the corrosion performance in GMW14872 and **Figure 35** shows ASTM B117 performance. Results here suggest that the organic acid-modified metal salt provided enhanced corrosion performance for the DIP system.

SUBSTRATE	PRIMER	TREATMENT	Avg.(mm)	Maximum (mm)
CRS	MLN1981	MLB875	2.8	4.6
CRS	MLN1981	MLB875	2.8	5.5
CRS	MLN1981	Chrome-free wash Primer wash Primer	2.3	7.0
CRS	MLN1981	Chrome-free wash Primer wash Primer	2.0	6.5
CRS	MLN1981	Immersion prototype	4.6	8.8
CRS	MLN1981	Immersion prototype	4.8	7.8
CRS	MLN1981	Spray-On/Rinse-Off	2.3	5.8
CRS	MLN1981	Spray-On/Rinse-Off	2.8	3.9
CRS	MLN1981	DIP with Zirconium & 0.5% Dihydroxybenzoic acid	15.2	18.7
CRS	MLN1981	DIP with Zirconium & 0.5% Dihydroxybenzoic acid	5.8	8.7
CRS	MLN1981	DIP with Zirconium & 0.5% diaminobenzoic acid	4.6	6.3
CRS	MLN1981	DIP with Zirconium & 0.5% diaminobenzoic acid	5.3	6.3
CRS	MLN1981	DIP Zirconium	0.8	2.0
CRS	MLN1981	DIP Zirconium	2.5	4.6
CRS	MLN1981	DIP Zr & cerium nitrate	0.8	1.5
CRS	MLN1981	DIP Zr & cerium nitrate	1.0	3.3
CRS	MLN1981	DIP Zirconium & ammonium molybdate	6.4	9.8
CRS	MLN1981	DIP Zirconium &ammonium Molybdate	1.5	6.4
CRS	MLN1981	DIP Zr & Organic acid-modified metal salt	1.0	2.3
CRS	MLN1981	DIP Zr & Organic acid-modified metal salt	1.0	2.5

Table 19. GMW14872 (40 cycles) Corrosion Performance of DIP formulations with metal salts and modified organic acids versus commercial controls on aluminum and CRS under MIL-DTL-53022B Type II solvent-borne epoxy primer.
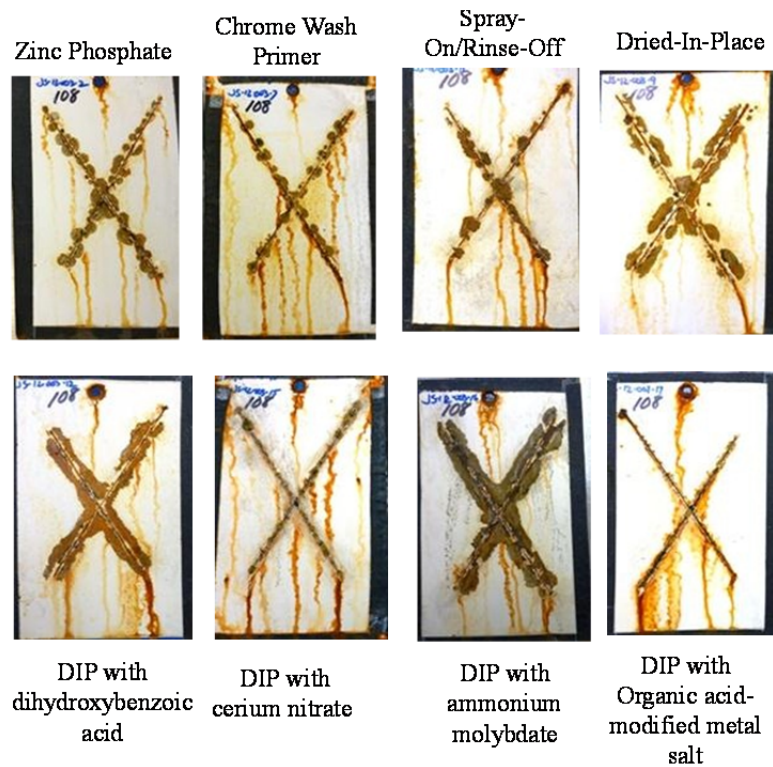
Figure 33: GMW14872 (40 cycles) Corrosion Performance of DIP zirconium formulations with metal salts and modified organic acids versus commercial controls on aluminum and CRS under MIL-DTL-53022B Type II solvent-borne epoxy primer
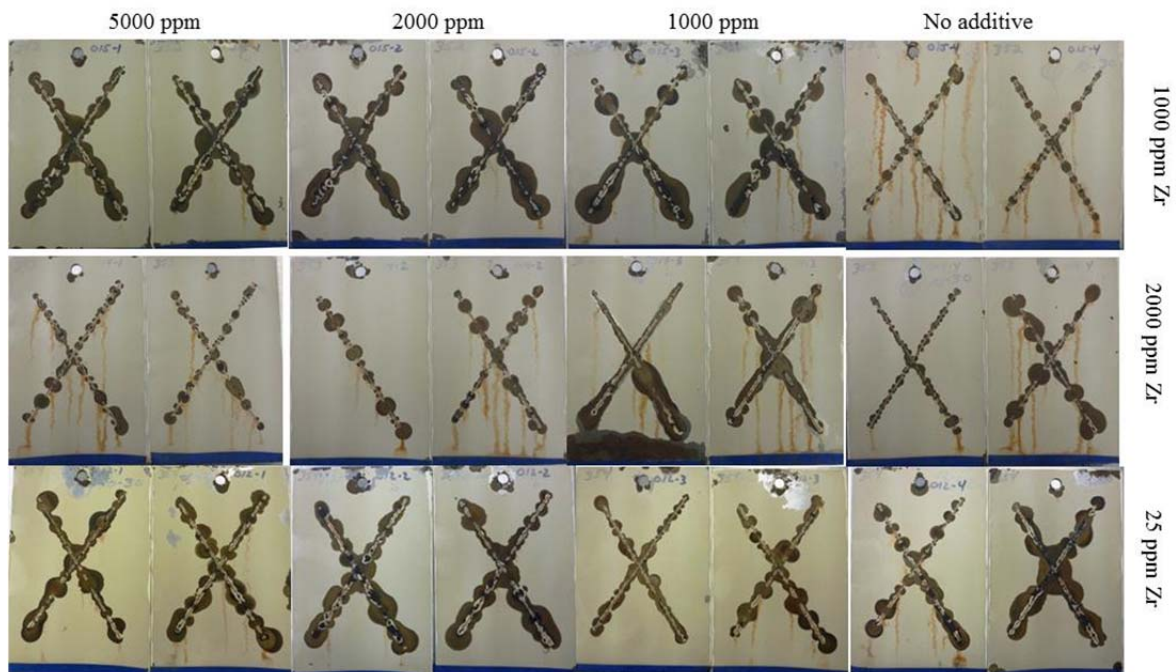
Figure 34. GMW14872(40 cycles) corrosion performance of zirconium Dried-In-Place treatment, modified with varying levels of organic acid-modified metal salt.
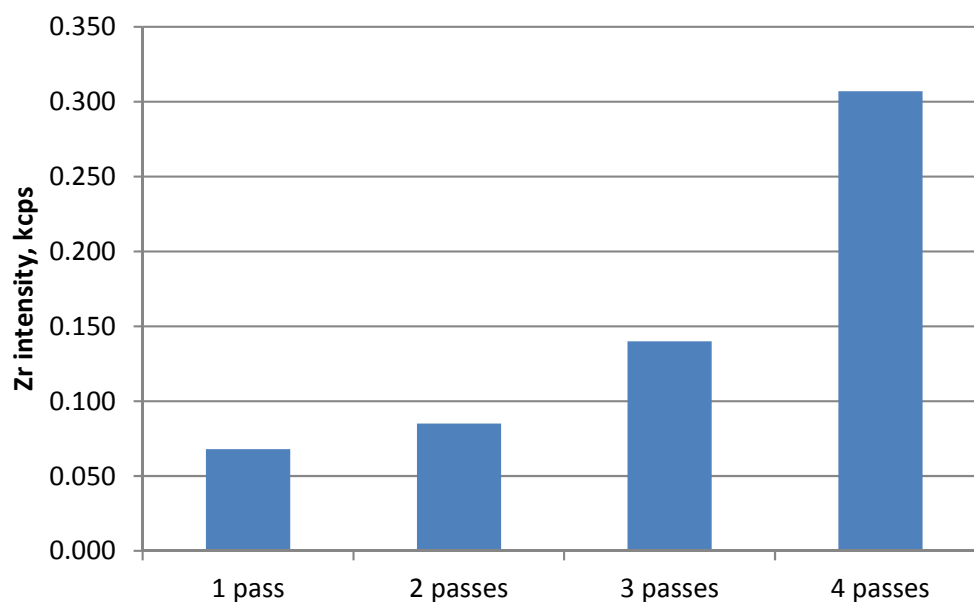
Figure 35. Zirconium intensity in kilocounts per second, when CRS panels are coated with a HPLV gun.

The system above was also characterized using XRF. Samples were coated using a High-Pressure/Low-Volume spray gun at 1 to 4 mist passes. The zirconium deposited was dependent on the number of passes. Comparative date for this is given in **Figure 36**.
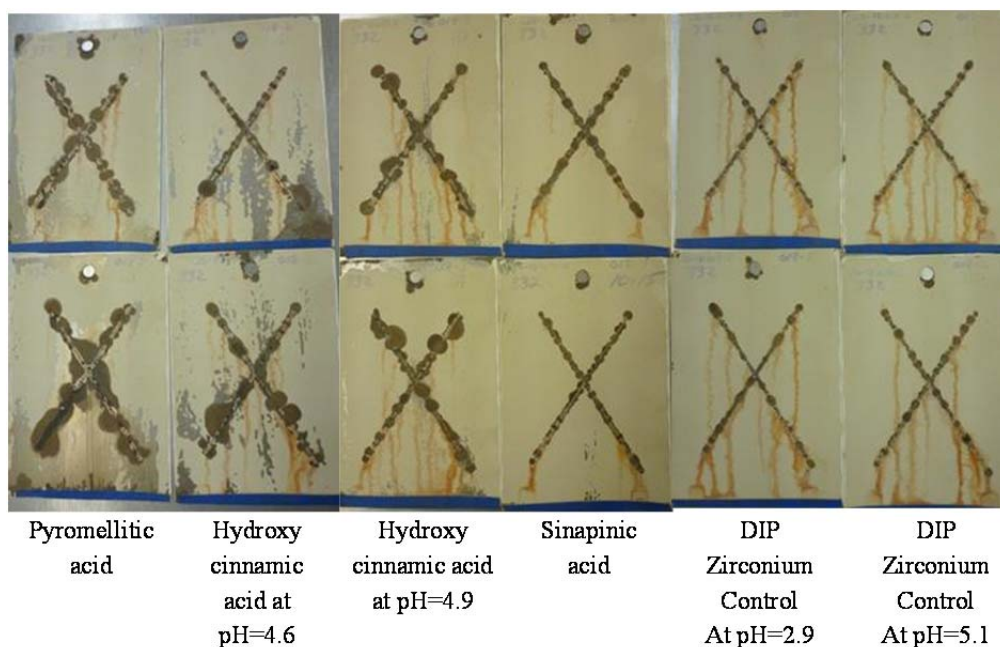
Figure 36: GMW14872 (40 cycles) corrosion performance of zirconium Dried-In-Place treatment, modified with hydroxyl-functional carboxylic acid additives

Additional work was conducted to determine if hydroxybenzoic acid compounds (known corrosion inhibitors) could improve the corrosion performance of the DIP formula. Experiments were carried out with other hydroxy-benzoic acid compounds. These included pyromellitic acid, hydroxycinnamic acid, and sinapinic acid.[26] A sodium hydroxide/potassium hydroxide solution was added to facilitate dissolution of the hydroxycinnamic acid sample due to low water solubility; however it should be noted that the mixture remained cloudy even after the modification. Samples were prepared and coated with MIL-DTL-53022B Type II solvent-borne epoxy primer, then placed into 40 cycles of GMW14872. In this test, no benefit was observed with the hydoxybenzoic acid derivatives (see **Figure 36**). No further work was done looking at hydroxy-functional carboxylic acid materials.

Finally an experiment was conducted to determine if the corrosion performance of the DIP pretreatment might be improved by using an alternate source of soluble zirconium (similar to experiments conducted in earlier tasks). This was achieved by adding zirconium orthosulfate, or zirconium oxynitrate at 200 ppm zirconium. The zirconium orthosulfate required additions of small amounts of fluoride added as either hexafluorozirconic acid, hexafluorotitanic acid or ammonium bifluoride to stay in solution. The sample prepared with hexafluorotitanic was buffered to a pH of 5.2. The zirconium oxynitrate was also only partially soluble in water and required the addition of hexafluorozirconic acid to stay in solution. Results from ASTM B117 salt spray corrosion show that the zirconium orthosulfate, dissolved with hexafluorotitanic acid gave slightly better corrosion resistance than the control DIP system and slightly worse than the zinc phosphate control. Photos of the salt spray corrosion panels are shown in **Figure 37**.

Several corrosion inhibitors were evaluated in this task to improve the performance of the DIP formula. In the benchmarking study DIP formula based on the prototype formula from Task 1, only more dilute to increase the pH were evaluated by ASTM B117 and GMW14872. Results from this study suggested that the formula performed similar to the Zircobond®4200 (no copper) immersion pretreatment and the zinc phosphate controls During this task a compound based on an organic acid-modified metal salt which acts as a cathodic and anodic inhibitor was identified which improves the performance of the DIP formulation. Results from this work suggest that a DIP formula is possible which would provide corrosion performance similar to control in GMW14872 and ASTM B117 corrosion testing.
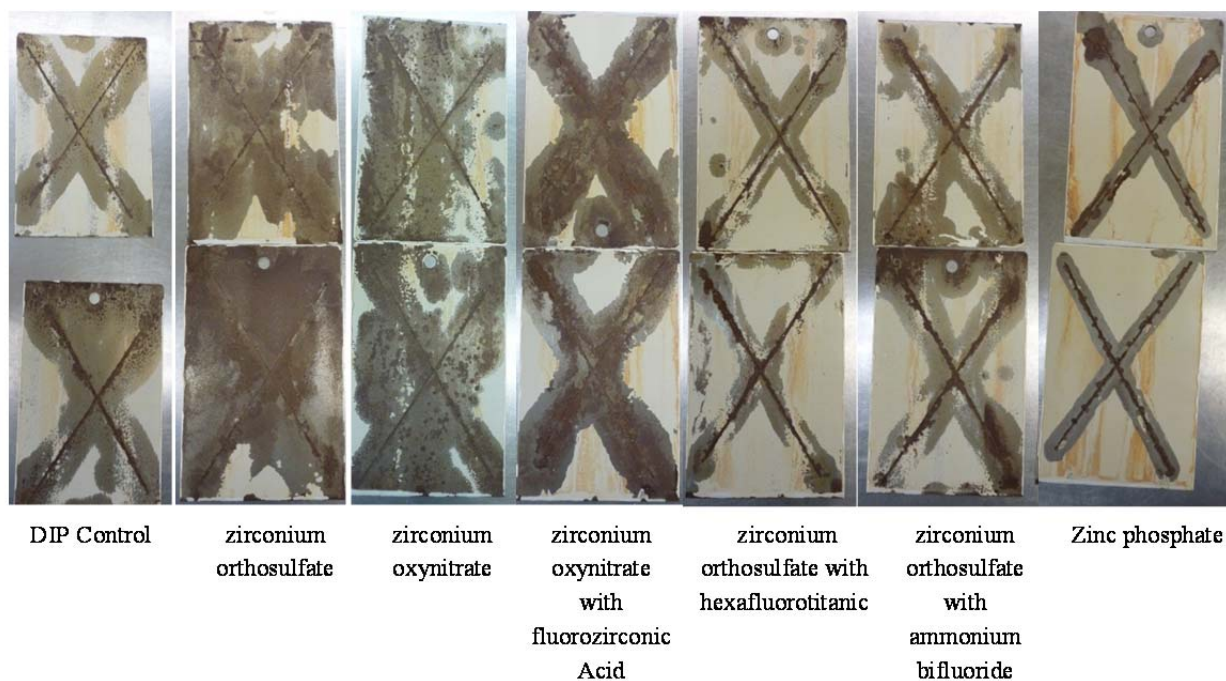
Figure 37. Salt Spray Corrosion Resistance of zirconium Dried-In-Place treatment made from alternate sources of zirconium.

4. Zirconium Oxide Toxicity Discussion

As specified in the contract, and prior to the experimental work of this project, a white paper was written that summarized the known potential health and environmental impacts of zirconium-based pretreatments. This white paper, entitled "Summary of the Potential Health and Environmental Impacts of Zirconium Based Pretreatments" (see Appendix 1) was drafted and submitted to SERDP personnel. The information contained in the white paper was based on current industry knowledge and on a literature review of the current information known about the pretreatment materials. The document was reviewed by technical, environmental, industrial hygiene, and toxicology professionals. The white paper concluded that zirconium pretreatments "provide improved health, safety, and environmental characteristics compared to the incumbent chromate- and zinc phosphate-based pretreatments. Environmental benefits include a reduction in energy consumption, water consumption, and sludge formation. Finally, zirconium-based pretreatments are used at lower bath concentrations and lower amounts of metal are deposited to substrate. This inherent property of zirconium pretreatments results in waste products that are less hazardous and significantly lower in volume than those resulting from traditional metal pretreatments."

Conclusions and Implications for Future Research / Implementation

Through the experimental portions of this project, the performance requirements for evaluation of zirconium pretreatment were guided by the Military specifications for the applied coatings, such as MIL-DTL-53030 and MIL-DTL-53022. These specifications were used to

outline most of the evaluation testing, such as corrosion, flexibility, solvent resistance, and water resistance.

More recently, however, a new revision of TT-C-490 has been published – TT-C-490F. This comprehensive specification now includes a *Type IV – Inorganic Pretreatment* designation, which outlines the submission guidelines and performance expectations for zirconium-based pretreatment products. The key performance requirements (corrosion resistance) for Type IV coatings per TT-C-490 are identical to the performance requirements outlined in the -53030 and -53022 primer specifications mentioned above.

PPG's zirconium oxide-based pretreatment technology, developed for original equipment manufacturing settings (Zircobond), was evaluated and tested over common substrates used in military assets. It was found in this testing that the current formulation, which was designed to function with electrocoat, would need to be modified to perform well under the more widely-used water- and solvent-borne chemical agent resistant coating systems. Performance improvements were made to meet the requirements and to ensure compatibility. A system based on Zircobond®4200 without the Cu additive was developed for use in an immersion process. The new formulation also varies from Zircobond®4200 in that it operates at a higher free fluoride level. Reduction in Cu level, and addition of 80 ppm free fluoride provided improved corrosion performance under the CARC coating system over commercial thin-film products based on zirconium. In DoD specification testing, these two improvements allow the immersion formulation to perform *similar to state-of-the-art tricationic zinc phosphate and chrome wash primer coating, as well as chrome (VI) pretreatments for aluminum*. Additionally, a spray OEM application was developed. In the case of the spray application, a small amount (10 ppm) of Cu additive, along with 80 ppm of free fluoride, was found to provide the best performance. This prototype has been shown to perform similar to controls in GMW14872 and ASTM B117 testing at 20 cycles and 336 hours salt spray, respectively. However, after 40 cycles GMW14872 and 1008 hours the control systems outperform the prototype spray system.

In addition to the Original Equipment Manufacturing setting, military assets frequently require recoating in depots and field service sites, where treatment by immersion is impractical. Under this project, two approaches were developed to facilitate the introduction of zirconium oxide-based pretreatment technology into these settings. In the first of these, a novel Spray-On/Rinse-Off prototype was developed which utilizes a non-Newtonian rheology modifier. The modifier allows spray application via conventional means, yet thickens on vertical surfaces for longer contact times and reduced run off. This system performed relatively well, showing a small decrease in adhesion testing and corrosion testing when compared to the tricationic zinc phosphate system. The second approach, which would be particularly suitable to field service sites, was to develop a sprayable prototype that eliminates the rinsing step and can be Dried-In-Place. This DIP formulation, as well as the other improvements found in task 3.3, performed quite well in corrosion testing. Performance in many tests for these systems was similar to that of a state-of-the-art tricationic zinc phosphate system or a chrome (VI)-based wash primer coating.

The technical goal of this project was to develop and optimize a zirconium-based surface treatment with the following attributes: 1) ease of application using existing spray and immersion

methods with minimal infrastructure modification, 2) performance equal to (or better than) existing chrome (VI) wash primer coatings, 3) broad compatibility with the current suite of military coatings (including solvent- and water-based primers and top coats), and 4) compatibility with a broad range of substrates. As the project evolved, particularly driven by visits to Letterkenny Army Depot and USMC Logistics Base Albany and interactions with DoD personnel, it was noted that zirconium pretreatment should be considered an alternative to zinc phosphate, rather than comparing it only against chrome (VI) wash primers.

For the immersion formulation, the above goals have largely been met. Ease of application, and both substrate and coating compatibility have all been amply demonstrated. In terms of performance, there are individual instances of immersion applied zirconium technology not quite matching the zinc phosphate or chrome wash primer controls. But overall, the capability of zirconium to meet established Mil-Spec performance requirements has been shown. Work is ongoing, at no cost to the contracting agency, to further optimize the immersion formulation for use in DoD applications. For spray and Dried-In-Place application, performance was similar to a tricationic zinc phosphate system or a chrome (VI)-based wash primer coating in some cases, and modestly lower-performing in others. Overall, performance similar to the incumbent technologies was achieved without the use of chrome (VI) or phosphate pretreatments. Reducing the use of these two technologies has several environmental and cost benefits. During the reaction of the zinc phosphate solution with metal substrates, an insoluble precipitate or sludge can be generated. This sludge typically contains compounds of iron, zinc, manganese, nickel, and phosphate, as well as oil. Due to the nickel (a regulated metal) content, special handling and disposal of the sludge is necessary. This special disposal process also creates additional costs which can be significant and add to the operational costs. Additional cost and environmental negatives are avoided by using the systems developed in this project as opposed to chrome-based coating systems.

The survey of depot sites during this project highlighted a direct need for a pretreatment such as the one developed as part of Task 1. Based on these project results, further development and demonstration opportunities are planned under ESTCP project WP-201318, with a goal of qualifying zirconium oxide-based pretreatment technology for use on Department of Defense assets. Ongoing exposure tests carried over from this project will also be monitored under WP-201318.

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- US ARMY Corrosion Summit, February 9-11, 2010 (seminar)
- 1109th Aviation Classification Repair Activity Depot Workshop, June 23, 2010 (seminar)
- TARDEC Paint Forum, February 1, 2011 (seminar)
- DoD Corrosion Conference, July 31 to August 5, 2011 (seminar/paper)
- ASETSDefense Conference, August 27-30, 2012

APPENDIX 1

SERDP 1676 W912HG-09-C-0038

Summary of the Potential Health and Environmental
Impacts of Zirconium Based Pretreatments

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Summary

Zirconium-based metal pretreatment technology is an alternative to conventional technologies such as zinc phosphate, chromate-containing etch primers, and chromate conversion coatings. Compared to these conventional technologies, zirconium-based pretreatments can provide the following advantages:

- Excellent corrosion protection and improved adhesion while operating under ambient conditions.
- Reduction in the amount, and toxicity, of waste materials generated from pretreatment application and disposal processes.
- Reduction in energy consumption, due to ambient operating conditions.
- Reduction in water use in the pretreatment process.
- Reduced exposure to toxic and regulated materials during the pretreatment process.
- Reduced deposition of metallic compounds that could be released during rework and other downstream operations.

With excellent corrosion protection and improved health, safety, and environmental effects, zirconium-based metal pretreatments provide an attractive alternative to conventional pretreatment technologies.

Background

Pretreatments are typically used to promote the adhesion of paint to metallic substrates and, for some products, provide a degree of corrosion inhibition. Three metal pretreatments used broadly by the Department of Defense and commercial interests are zinc phosphates, chromate-based wash primers, and chromate-based conversion coatings. A general description of pretreatment bath chemistries and processing parameters is given below.

Zinc phosphate is used, primarily, to enhance the corrosion performance of steel. The current state-of-art in metal zinc phosphating is known as tricationic zinc phosphate.[1] Addition of cations, supplemental to zinc, enhance the growth of a homogenous crystal surface conducive to paint adhesion. These cations typically include one or more of the following: nickel, cobalt, manganese, tungsten, etc.[1] at pretreatment bath concentrations ranging from 200-1000 ppm and zinc at a concentration of 900-2500 ppm. A typical zinc phosphate bath is operated at pH = 3.0-3.5, 125°F and is applied by spray or immersion. The zinc phosphate coatings have a typical film thickness of 3-5 microns.

As an alternative to zinc phosphate pretreatments, chromate-based etch primers may be used to coat a range of substrates. Chromate-based etch primers were originally developed as a substitute for zinc phosphating for ship building.[2] Etch, or wash, primers are typically acidic in nature and contain a chromium complex, at a concentration of approximately 5000 ppm, in an alcoholic polyvinyl butyral solution. Additionally, these systems use a phosphoric acid based catalyst.[3] Etch primers are typically spray or brush applied to a final film thickness of 75-125 microns. In addition to chromate based etch primers, chromate based conversion coatings are broadly used by the aerospace industry.[4] The chromium oxide coating is formed from chromic acid and accelerants such as potassium ferricyanide. A typical bath contains about 1500 ppm Chromium

and is run at pH 1-2, 80°F. The chromic oxide coating is approximately 1.2 microns in thickness.

Zirconium-based Metal Pretreatments

As an alternative to zinc phosphate and chromate based coatings, hexafluorozirconium complexes (X_2ZrF_6, where X = K or H) have been used to treat metal for more than a quarter of a century.[5-6] Hexafluorozirconium complexes are used in a number of industrial and consumer settings. Fluorozirconic acid is used in metal cleaning and finishing, while the fluorozirconate salts are used in abrasives, aluminum production, ceramics, glass manufacturing, and in the preparation of fluxes. However, the largest consumption of fluorozirconates is to impart fire retardant properties to wool-based products including airplane upholstery and children's clothing.[7]

More recently, a number of X_2ZrF_6-based pretreatments have been developed, and patented, for use on aluminum and galvanized substrates.[8-9] Broad substrate applicability has only been achieved recently with the advent of a new cationic additive technology to promote corrosion protection on steel. This technology also promotes uniform film formation at ambient temperatures and short contact times. X_2ZrF_6-based pretreatment baths are operated at ~80°F, at a pH of 4.5-5.0. The bath consists of 50-500 ppm Zirconium, which is applied either by immersion or spray. The zirconium oxide coatings have film thicknesses of 0.01-0.20 microns.

When considering the typical deposition levels of phosphate, chromate, and zirconate pretreatments, the amount of zirconium deposited to the substrate per unit area is roughly an order of magnitude lower than the typical amounts of the metals deposited from the other processes. Thus, the potential for exposure to the incorporated pretreatment metals during subsequent operations, such as sanding, would be reduced by a corresponding amount.

Routes of Zirconium Exposure

Three potential sources of exposure to pretreatment materials are exposure to the bath and bath makeup solution, coating exposure, and exposure to released waste products as the result of the coating application.

The bath chemistry of a typical zirconium-based pretreatment consists of >99.9% H_2O (by weight) with the remaining constituents consisting of hexafluorozirconic acid (H_2ZrF_6) and proprietary additives at a pH = 4.8. Therefore the component with the highest concentration, other than H_2O, is H_2ZrF_6 found in a typical operating bath at <0.1%. The makeup solution of the aforementioned bath consists of >98.5% (by weight) H_2O at a pH = 2. The reaction of the dilute H_2ZrF_6 bath with substrate results in a ligand metathesis with alkaline sites on the substrate surface. The final coating consists of 0.01-0.20 microns of zirconium oxide. Potential exposure to zirconium may also occur if the adhered zirconium oxide is released into the work environment through activities such as sanding. Although sanding is not specified as part of the standard application of zirconium-based pretreatments, it may be required where rework becomes necessary.

The final source of environmental impact is though material discard and remediation. This is a topic of high priority in the metal pretreatment industry due to the toxic nature of many of the

conventional metal pretreatment systems. Incumbent technologies include regulated metal and phosphate components that require special waste release controls. These regulations were initially developed under the Clean Water Act of 1977 and have been further defined by the United States Environmental Protection Agency.[10-11] This legislation sets limits on waste release and requires additional treatment before discharge.

Zirconium Toxicity

The toxicity of zirconium compounds in model ecological systems has been evaluated by Couture et al.[12] This research concluded "that zirconium presents a low potential for environmental concern." Further clarification of the nonhazardous nature of zirconium-based pretreatment waste products was obtained from USEPA.[13] A letter was submitted to the Director of the Office of Solid waste at the USEPA, on behalf of the Alliance of Automobile Manufactures, for "a determination that the use of the zirconium oxide coating process, as part of coating operation on automotive bodies containing aluminum (when treating aluminum substrates there is a modest increase in insoluble material due to the formation of AlF_x) would not cause downstream wastewater treatment sludge to be classified as hazardous waste F019."* The response, from Matt Hale (Director of the Office of Resource Conservation and Recovery), concludes that "the use of this coating process would not generate a wastewater treatment sludge classified as EPA Hazardous Waste code F019."[13]

There have been mixed reports regarding the effects of inhalation exposure to dusts containing zirconium compounds. Marcus et al. reports that workers with up to 30 years exposure to zirconium compound dust show no statistically relevant loss of lung function or observed changes in chest radiographs.[14] Bartter et al. and Werfel et al., however, report pulmonary granulomas in workers chronically exposed to dusts of zirconium compounds.[15-16] OSHA and ACGIH® have established an airborne exposure limit for zirconium compounds of 5 mg/m^3 time weighted average (TWA) (see **Table 1**). In this application, zirconium replaces hexavalent chromium, which has a 0.005 mg/m^3 time weighted average (TWA) exposure limit. In addition, the OSHA standard[17] imposes a number of additional requirements (e.g., medical surveillance, training) when hexavalent chromium is used in the workplace.

Table 1: Airborne exposure levels for zirconium compounds and inorganic fluoride.

	ACGIH®[a]		OSHA[b]		NIOSH[c]	
	as Zr	as F	as Zr	as F	as Zr	as F
TWA[d]	5 mg/m^3	2.5 mg/m^3	5 mg/m^3	2.5 mg/m^3	5 mg/m^3	2.5 mg/m^3
STEL[e]	10 mg/m^3	-	-	-	10 mg/m^3	5 mg/m^3

[a] American Conference of Governmental Industrial Hygienists. [b] Occupational Safety and Health Administration.
[c] National Institute for Occupational Safety and Health. [d] Time weighted average. [e] Short term exposure limit.
All data from reference 18.

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* F019 is an EPA F-code resource conservation and recovery act hazardous waste listing. The listing includes wastes generated from common industrial and manufacturing processes.

Zirconium complexes, along with inorganic fluorides, have well established occupational exposure limits. The recommended exposure limits for zirconium and fluoride are given in **Table 1** (For additional safety and health precautions regarding material handling, refer to the product material safety data sheet).[19] However, *zirconium oxide* is generally regarded as having low systemic toxicity at pH values normally associated with biological activity. This is due to the insoluble nature of zirconium dioxide which makes it physiologically inert.[20]

In contrast with the foregoing information demonstrating the lower toxicity of zirconium-based metal pretreatments, the intrinsic toxicity of chromate-based metal pretreatments has been well established. The World Health Organization has reported that "there is sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, zinc chromates, strontium chromate and lead chromates." The International Agency for Research on Cancer has classified these chromium(VI) compounds as Class I carcinogens.[21]

Conclusion

Zirconium-based pretreatments provide improved health, safety, and environmental characteristics compared to the incumbent chromate- and zinc phosphate-based pretreatments. Environmental benefits include a reduction in energy consumption, water consumption, and sludge formation. Finally, zirconium-based pretreatments are less toxic than conventional pretreatment systems, such as chromates and zinc phosphate systems, are used at a lower bath concentrations and at lower amounts of metal deposited to substrate, and result in waste products that are less hazardous than those resulting from traditional metal pretreatments.

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